

Time Reversal Symmetry in Nonlinear Optics

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To my parents

Abstract

Results following from time reversal symmetry are developed for those nonlinear optical processes where a statistical average is required. This extends results found in Rayleigh (and Raman) scattering to nonlinear optical processes of arbitrary order, and generalises those few analyses specific to nonlinear optics. For example, Onsager relations for self-conjugate nonlinear optical processes (when input and output photons form degenerate pairs) are derived, and associated reversality relations generalised. In the nonresonant limit magnetic dipole but not electric quadrupole terms in coherent processes are suppressed. For this and other selection rules a careful treatment is required to obtain gauge invariant conclusions since the relevant electronic operators in multipolar and Coulomb gauges have differing time reversal signatures. For general processes purely electric dipole contributions to natural optical activity are possible when intermediate resonances are present; strong resonances are not required for the domination of this contribution over the traditional contribution. Time reversal symmetry may be used to show the prescription for assigning signs to phenomenological damping factors that is usually associated with the optical susceptibility formalism is incorrect. An experimental test based on electrooptic rotation in fluid media is proposed which may distinguish between this incorrect prescription and the correct prescription. The role time reversal symmetry plays in restricting the number of parameters in Judd-Ofelt theory is elucidated.

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1. Introduction

There are no mystical notions involved in time reversal – Gottfried [48].

1.1 Preamble

Beginning with Wigner's 1932 paper [139], the physics of time reversal has impacted on almost all areas of quantum theory. In this thesis we examine the consequences for nonlinear optics.

Probably the most widely known result associated with time reversal (T) symmetry is the 1964 experiment in which indirect evidence was found for its global violation [50]. It was demonstrated that kaon decay violates CP symmetry, where C is charge conjugation and P is parity. This, together with the requirement that the combined operations of C, P and T must be a symmetry of any theory (the CPT theorem), requires that T be violated. This effect is not predicted by the standard electroweak theory and no conclusive explanation for the violation exists [50]. The continuing search for direct evidence of time reversal violation is testament to the profound nature of the discovery [49]. In contrast to these complexities, electrodynamics is globally time reversally symmetric. Therefore, subtleties associated with the interpretation of such weak interaction experiments may be dispensed with [118]. Further, because electrodynamics has both a classical and quantum description, the correspondence principle allows our concepts of time reversal to be based on classical ideas, which are intuitively clear [48, 119].

Because electrodynamics is time reversally symmetric, the transition rates for time reversally conjugate (T-conjugate) light scattering processes are equal. For example, at the lowest order, where only one photon is involved, the rate of absorption is equal to the rate of emission. At the next order time reversal symmetry relates the Rayleigh scattering processes where the in and out photons are interchanged. These two equivalences have been known for many years and the consequences which follow have been examined extensively by various workers. This has led to the development of many useful results (see for example Refs. [1, 83, 103]).

The equivalences between T-conjugate nonlinear optical processes have also been known for many years. For example, the rate of second-harmonic generation is

equal to the rate of parametric down-conversion. However, in contrast to the linear case, the consequences that follow have received relatively little attention. With the explosion in nonlinear optics in recent decades, many applications of time reversal symmetry undoubtedly remain to be discovered and exploited. We present here a further step into these general issues. In particular, we extend results found in Rayleigh (and Raman) scattering to nonlinear optical processes of arbitrary order and generalise those few analyses specific to nonlinear optics.

1.2 Layout of thesis

Chapter 2 sets the scene for the thesis. We introduce the concepts of time reversal and time reversal symmetry and emphasise, via analogies with classical mechanics, that “there are no mystical notions involved”. The field of nonlinear optics is then briefly reviewed. Having introduced the two main components of this thesis we discuss the specific quantity to which time reversal will be later applied, namely the light scattering intensity. In particular, we examine in detail the Golden Rule expression for the nonlinear optical interaction of a system of identical particles (e.g. molecules, atoms, electrons) with a quantised radiation field. By assuming the particles are independent this intensity is rewritten in terms of one-particle transition amplitudes. We explicitly carry out this simplification because standard treatments appear not to adequately handle degeneracies in the particles’ initial and final states. Because these one-particle amplitudes are found from a perturbation-theoretic approach, we assume throughout this thesis that the electromagnetic fields are not very intense and that no strong intermediate resonances are present. To present clearly the results of the following chapters we develop a suitable notation for these amplitudes; the optical susceptibility notation is too cumbersome for our purposes. Finally, we outline the well established, but not widely known, gauge invariant formulation of quantum mechanics. This is in preparation for a later discussion (Chap. 4) where some of our results may appear at first glance to be gauge dependent.

In the first half of Chap. 3 we combine the ideas discussed in Chap. 2. In particular, we apply time reversal symmetry to the transition amplitude of a general nonlinear optical process. This leads to three reversality theorems (only one of these expresses time reversal, the other two represent the two separate components of the time reversal operation). These theorems have been known for many years; our contribution is to incorporate phenomenological damping factors. This generalisation is crucial since in later sections and chapters we wish to consider nonlinear optical processes which involve intermediate resonances. We also discuss phase conventions relating to the action of time reversal on the photon field, and conclude that a nonstandard convention gives the simplest expressions.

The reciprocal relations of Onsager [109, 110] provide useful index symmetries on the dielectric tensor [38]. Although nonlinear reciprocity relations have been discussed previously [52], to our knowledge Onsager relations on nonlinear op-

tical tensors have not yet been formulated. We present in the second half of Chap. 3 relations applicable to those coherent processes in which each input photon is degenerate with an output photon and vice versa. We term such processes self-conjugate; examples include Rayleigh scattering and those four wave mixing processes in which the two output photons have identical energies to the two input photons. As in the case of the Onsager relations on the dielectric tensor, our derivation is based on time reversal symmetry together with a summation over the possibly degenerate initial and final states, consistent with a statistical average. Incidentally, in contexts outside optics Onsager relations have been considered for situations where microscopic reversibility and equilibrium conditions do not hold [44, 45, 39].

Our analysis is used to address a recent discussion over the validity of the Onsager relations in GaAs. Bungay *et al.* [22] and Zheludev *et al.* [143] claim the relations in GaAs are violated by the presence of spin-orbit coupling. Etchegoin *et al.* [38], noting the spin-orbit interaction is time-even and does not affect statistical averages, argue against this. We give further support to this conclusion.

Chapter 4 discusses the time reversal selection rules which follow when the nonresonant limit is valid. (The nonresonant limit implies that all the photon energies are small in comparison with the relevant electronic transition energies.) For example, we find that for arbitrary order processes transitions between T-conjugate states in Kramers systems are suppressed in the electric dipole approximation; this generalises a rule found in Rayleigh scattering [15, 127]. Also, the magnetic dipole terms in coherent processes are suppressed whereas the electric quadrupole terms are not. In the nonresonant limit this modifies the belief that magnetic dipole terms are generally an order of magnitude larger than the electric quadrupole terms (e.g. Cao and Zhu [28]). These and other rules allow for an estimation of the relative importance of the various multipole contributions in the nonresonant limit. We also verify that identical results are found in both the multipolar and Coulomb gauges. Our aim in working this through is not to reopen the long-standing debate in the 1970s and 1980s over the relative merits of these gauge choices [18], but to use the conclusions of that debate in a novel field of application. Because the time reversal properties of the interaction Hamiltonians in the two gauges are different, and so apparently lead to incompatible selection rules, it is important to demonstrate and explain the gauge independence of time reversal selection rules.

Motivated by its possible use as a tool for probing chiral surfaces, there has been recent interest in natural optical activity in surface second-harmonic generation (Byers *et al.* [27], Kauranen *et al.* [75], Maki *et al.* [97]). (Natural optical activity is where the light scattering intensity changes if the handedness of polarisation of each photon is reversed.) Natural optical activity, whether in linear or nonlinear optics, has traditionally been thought to require the interference of electric and magnetic dipole terms [10, 79, 135]. The analysis of Byers *et al.* [27] has demonstrated that if intermediate resonances are present, purely electric dipole contributions to natural optical activity in second-harmonic generation are possi-

ble (without any need for an external magnetic field). Hecht and Barron [62] have extended this to Rayleigh and Raman scattering. Basing our analysis on time reversal symmetry, in Chap. 5 we give a natural optical activity expression for a general nonlinear optical processes. This symmetry has been used in previous analyses of optical activity (e.g. Hecht and Barron [62]); we follow Stedman [130] in particular. In agreement with previous discussions [27, 62], we find that in the presence of strong intermediate resonances the purely electric dipole contributions to natural optical activity dominate over the traditional terms. For moderate resonances we find that the electric dipole contributions are still of importance, contrary to the claims of Kauranen *et al.* [75] and Maki *et al.* [97]. We consider as an example natural optical activity in resonant two photon absorption, and discuss how it ought to be possible to combine the experimental methods of Gunde and Richardson [54] and Huang *et al.* [64] to measure the effect. Finally, we discuss some surprising modifications to standard parity selection rules which result when the purely electric dipole contributions are involved.

When a nonlinear optical process involves intermediate resonances it is necessary to include damping in the theory to properly account for the finite (rather than infinite) optical amplification. However, apart from a few simple cases there are considerable difficulties associated with the treatment of optical damping in a non-phenomenological manner, and commonly only a phenomenological treatment is tractable. The standard phenomenological approach is to include in the energy denominator parts of transition amplitude imaginary addenda [23]. The magnitude of each imaginary addendum carries the physically significant connotation of the lifetime of an excited state, and leads to Lorentzian lineshapes of appropriate and experimentally determinable width. In Chap. 6 we consider the restrictions time reversal symmetry places on the signs that may be associated with these addenda. This analysis, in combination with certain non-phenomenological discussions of damping [8, 34], leads us to adopt a prescription where the signs are all identical. This prescription is inequivalent to the most commonly employed prescription, which is usually associated with the optical susceptibility formalism [19, 23, 41, 87, 121]. We show that this later prescription is incompatible with time reversal symmetry and is therefore incorrect. Although in most cases the difference in results found under the two prescriptions is small, in a few cases qualitatively different predictions can arise. We show that electrooptic rotation is an example. We propose an experimental test based on this process which can realistically distinguish between the two prescriptions.

In many light scattering processes of physical interest the transition amplitude cannot be directly evaluated because the eigenvalue and eigenvector equations for the electronic subsystem cannot be solved exactly. For one photon absorption in lanthanide ions in solids Judd [68] and Ofelt [108] have overcome this problem by developing a parameterisation for the absorption intensities. This Judd-Ofelt theory involves expressing the transition amplitude as a matrix element of an effective operator and expanding this operator as a sum of spherical tensors. Various arguments have been used to show these spherical tensors must be of even rank. In Chap. 7 we show that time reversal symmetry gives a simple and

general proof of this result; this extends the analysis of Wang and Stedman [137]. We consider the surprising modifications to Judd-Ofelt theory which result when the Coulomb gauge is employed, and conclude that previous analyses in this gauge are incorrect [114, 137].

Throughout this thesis, unless otherwise specified, we work in the multipolar gauge, all multipole terms are included, and intermediate resonances are allowed for by the use of phenomenological damping factors. We note here that Chaps. 2 to 5 are based on Naguleswaran and Stedman [104, 105] and Chap. 6 is based on parts of Andrews *et al.* [8], rather than continuously reference these papers throughout. The results of this thesis are summarised in Chap. 8.

2. Background theory

In this chapter we discuss the theory and basic expressions that will be employed in this thesis. We first introduce the concept of time reversal and very briefly review the field of nonlinear optics (§§2.1 and 2.2). We then examine the light scattering intensity expression for a general nonlinear optical process, and develop an associated notation that is convenient for our purposes (§§2.3 and 2.4). Finally, a discussion is given for the transformation from the multipolar to the Coulomb gauge (§2.5).

2.1 Time reversal symmetry

We present here an introduction to time reversal and time reversal symmetry that is tailored to our purpose, i.e. to the nonrelativistic quantum theory of light-matter interactions (rather than to the quantum field theories involved in the standard model). For clarity these concepts are introduced in the classical case before giving their quantum mechanical description. Good references for the following material are the book of Sachs [118] “The Physics of Time Reversal”, and the quantum mechanics texts of Gottfried [48] and Sakurai [119].

2.1.1 Classical mechanics

The term time reversal is in fact a misnomer; it conjures images of going backwards in time. In classical mechanics the operation reverses the motion of all particles that constitute the system. A better term would therefore be motion reversal [1, 119], but we revert to the usual usage. Time reversal symmetry refers to the behaviour of the system after time reversal: A time reversally symmetric system will retrace its path upon reversing all its velocities. These two concepts are best illustrated by an example.

Consider a classical particle whose state at time t_0 is specified by position $\mathbf{r}(t_0)$ and velocity $\mathbf{v}(t_0)$ (Fig. 2.1). Suppose this particle evolves for a time t_1 , reaching position and velocity $\mathbf{r}(t_1 + t_0), \mathbf{v}(t_1 + t_0)$ (case I). At this time $t_1 + t_0$ time reversal is applied so that the position is unchanged but the velocity is reversed: $\mathbf{v}(t_1 + t_0) \rightarrow -\mathbf{v}(t_1 + t_0)$. The particle then evolves for another time interval t_1 .

If at $2t_1 + t_0$ the particle has returned to its original position: $\mathbf{r}(2t_1 + t_0) = \mathbf{r}(t_0)$ with opposite velocity: $\mathbf{v}(2t_1 + t_0) = -\mathbf{v}(t_0)$, and if this is true for an arbitrary t_0 and t_1 , then the system is said to be time reversally symmetric (case II, which looks like a film of case I run backwards). This would not be the case if for example external magnetic fields or frictional forces were present, but is always the case for closed systems in classical mechanics.

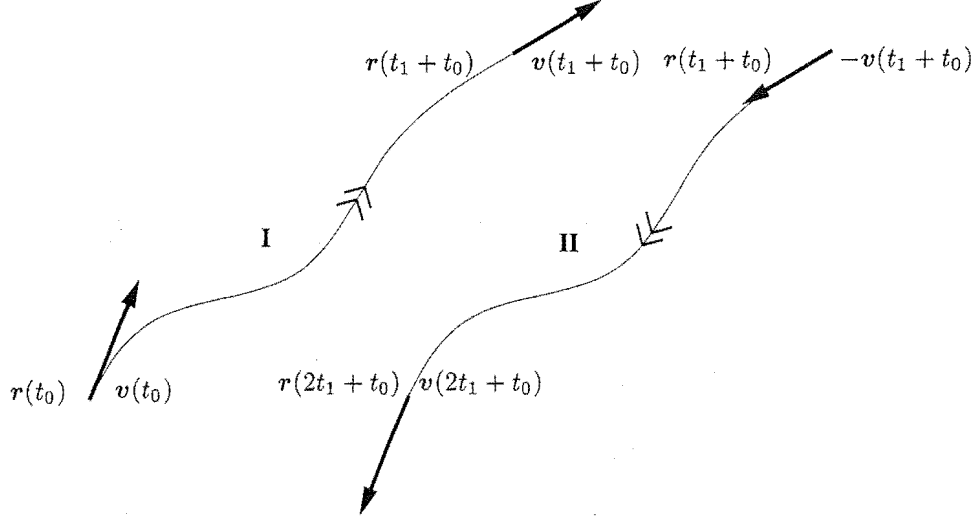


Fig. 2.1: Case I illustrates the path of a classical particle that has evolved for a time interval t_1 . Time (i.e. motion) reversal is applied at $t_1 + t_0$. Case II illustrates the particles' subsequent path as it evolves for another interval t_1 . If case II corresponds to case I 'running backwards', then the system is time reversally symmetric.

For large scale organised systems time reversal symmetry is never observed. For example, a stack of blocks may topple over but scattering blocks onto a table will not result in those blocks falling on top of one another to form a stack. This apparent irreversibility does not reflect a lack of time reversal symmetry but is due to the complex nature of the initial and final states involved. The ability to motion reverse a large system is severely restricted by the vast number of parameters needed to precisely specify such a state. Therefore, although in principle it is possible to observe time reversal symmetry in such cases, in practice it is not feasible [118].

Lee [85] argues that such difficulties may in fact be encountered in microscopic quantum systems involving only a few particles if complex phase relationships exist between those particles. In this thesis we use the number state basis for the photon field so that such questions of phase do not arise and our microscopic quantum processes are readily reversible. Further, results that follow from time reversal symmetry do not depend on the difficulty with which the process may be reversed in the laboratory, but follow only from the knowledge that if this reversed process were (somehow) arranged then its rate would be the same as the original.

This idea that complex states can lead to (an apparent) irreversibility was expanded upon by Boltzmann in the last century in an attempt to explain why entropy increases even though the underlying motions are time reversally symmetric. He argued that if a complex system (such as the universe) was started off in a privileged part of phase space, then because of this complex nature it is highly likely to evolve toward equilibrium rather than away from it. This gives a forward sense of time. A more complete description of what fixes the arrow of time is one of the open questions in physics, touching on such fundamental issues as the origin of the universe [55]. Note, because this arrow is independent of the physics of time reversal [118], such issues need not be considered in this thesis.

For a closed system in classical mechanics time reversal symmetry is always built into the equations of motion. As shown by Fig. 2.1, it follows that if $(\mathbf{r}(t), \mathbf{v}(t))$ is a solution, then $(\mathbf{r}(-t), -\mathbf{v}(-t))$ is a solution to the reversed equations. Beyond this there are very few cases where the symmetry is used directly in the solution to dynamical problems [118]; it is in the quantum mechanical case where the symmetry becomes a rich source of information.

2.1.2 Quantum mechanics

In quantum mechanics time reversal is represented by an operator T . Because light-matter interactions have both a classical and quantum description, the correspondence principle requires T to effect a similar reversal as in the classical theory. In particular, because the state of a classical particle transforms under time reversal as $(\mathbf{r}, \mathbf{v}) \rightarrow (\mathbf{r}, -\mathbf{v})$, $|\bar{\phi}\rangle \equiv T|\phi\rangle$ must be the motion reversed state with respect to $|\phi\rangle$. Also in analogy with the classical case, a quantum system is time reversally symmetric if the wavefunction retraces its path upon the application of T (Fig. 2.2). We now consider the form such an operator must take.

The time reversal operator is antilinear: $TiT^{-1} = -i$, and therefore is distinct from most other operators in quantum mechanics. Because the position and momentum operators are time-even and time-odd respectively: $T\mathbf{r}T^{-1} = \mathbf{r}$ $T\mathbf{p}T^{-1} = -\mathbf{p}$, this antilinearity is required to preserve the fundamental commutation relation $[r_i, p_j] = i\hbar\delta_{ij}$. Because $T^2|\phi\rangle \propto |\phi\rangle$, T is then antiunitary [48] and may be written UK , where U is unitary and K is the complex-conjugation operator. This K operation is basis dependent and therefore U contains a counterbalancing part W that reverses all time-odd quantities (e.g. $W|\mathbf{p}\rangle = |-\mathbf{p}\rangle$), so that T is basis independent. To preserve the angular momentum commutation relation $[J_i, J_j] = i\hbar\epsilon_{ijk}J_k$, the Pauli matrices must be time-odd $T\boldsymbol{\sigma}T^{-1} = -\boldsymbol{\sigma}$, and U includes σ_y . Denoting this spinorial operation S , the time reversal operator therefore takes the form

$$T = SWK. \quad (2.1)$$

Equation (2.1) may be used to show $T^2|jm\rangle = (-1)^{2j}|jm\rangle$ [118], i.e. T^2 is 1 if the system has integer values of total angular momentum and is -1 for half integer values. In this second case $|\bar{\phi}\rangle$ is distinct and orthogonal to $|\phi\rangle$.

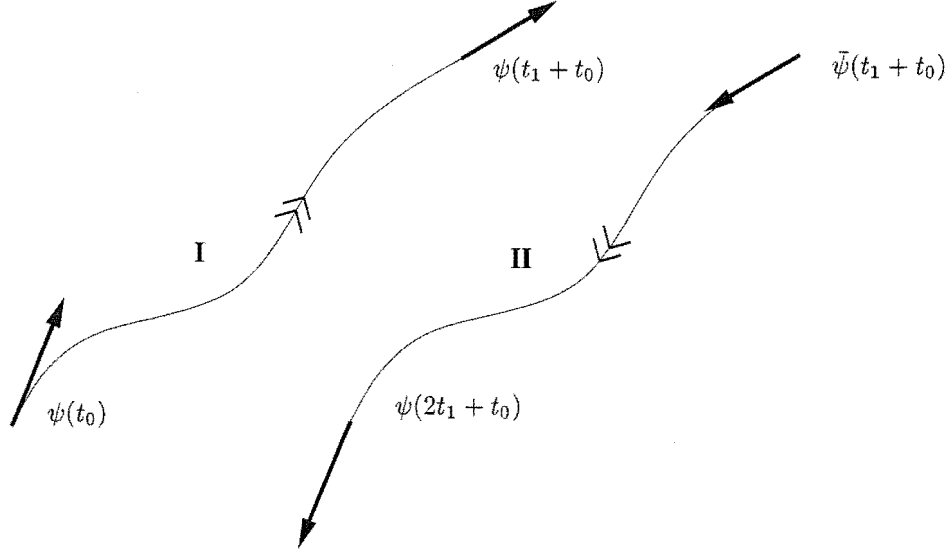


Fig. 2.2: Case I illustrates the evolution of a wavefunction for a period t_1 . Time reversal T is applied at $t_1 + t_0$. Case II illustrates the wavefunctions' subsequent path as it evolves for another interval t_1 . In analogy with Fig. 2.1, if $\psi(2t_1 + t_0)$ is the motion reversed state with respect to $\psi(t_0)$, the system is time reversally symmetric.

Because it is sufficient for our purposes, we assume throughout this thesis that the Hamiltonian is time-independent; see Johnsson [67] for a discussion of the general case. Further, unless otherwise specified, we assume no time-odd interactions are present (such as those due to external magnetic fields). In this case the inequivalence of T -conjugate states for odd j (Kramers) systems manifests itself as the well known Kramers degeneracy. This was originally shown by Wigner [139], who first introduced time reversal into quantum mechanics.

If $|\psi(t)\rangle$ is a solution to the Schrödinger equation, then it follows directly from the application of T that $|\bar{\psi}(t)\rangle = T|\psi(t)\rangle$ is a solution of the 'time reversed' Schrödinger equation, i.e. the Schrödinger equation with $t \rightarrow -t$ [102, 119]. Likewise, if $\mathcal{O}_H(t)$ satisfies the Heisenberg equation for the operator \mathcal{O} , then $\bar{\mathcal{O}}_H(t) = T\mathcal{O}_H(t)T^{-1}$ satisfies the reversed Heisenberg equation [85]. These results are in direct analogy with the classical case, as required by the correspondence principle.

Unlike most authors (Refs. [1, 20, 29, 48, 83, 85, 101, 102, 119, 118]), certain authors (Refs. [13, 63, 72]) include in T the operation $t \rightarrow -t$. In this case it no longer follows from T that $|\bar{\psi}(t)\rangle$ and $\bar{\mathcal{O}}_H(t)$ are solutions of the reversed equations. For this reason we prefer $t \rightarrow t$ over $t \rightarrow -t$ (see also §6.2.3). Note, many results following from time reversal symmetry, including those derived here, are unaffected by this. In particular, the application of T to Golden Rule expressions is unaffected because the time variable does not appear explicitly.

2.2 Nonlinear optics

2.2.1 Preamble

To observe the nonlinear interaction of light with matter either high intensity radiation or resonance enhancement is required. Because of this, nonlinear optical phenomena play no part in the natural world. It was not until 1961, with the advent of lasers, that the first nonlinear optical process (second-harmonic generation) was observed [42]. Subsequently the field of nonlinear optics has received a tremendous amount of attention, leading to important applications in many branches of science and engineering.

Much of the current research in nonlinear optics is driven by the new technology of photonics. By employing light beams rather than electrical currents this technology aims to transfer information at speeds faster than is possible using electronics [66]. This requires nonlinear optical processes such as second-harmonic generation and four wave mixing [23]. To optimise such processes, a great deal of research has gone into the design of commercial nonlinear optical materials [122]. For example, organic and polymer materials that have delocalised, multicentre bonds have been considered because of their strong response to light [46]. Also considered are the dynamical nonlinearities in semiconductors, where the promotion of electrons from the valence band to the conduction band dictates the subsequent absorption and refractive index properties of the semiconductor [23, 47].

Other areas of research involving nonlinear optics include nonlinear spectroscopy [87] and the use of second-harmonic generation as a surface-specific probe [112]. Second-harmonic generation is also important as a tool in generating coherent output at frequencies for which there are no convenient laser sources [40].

Because of these and other applications nonlinear optics will remain a fruitful area of research for many years to come.

2.2.2 Standard formulation

The interaction of light with matter induces oscillating dipole moments within the constituent particles of the matter. The standard formulation of both linear and nonlinear optics involves writing this time-dependent material polarisation as a function of the electromagnetic field amplitudes. All the required observables are then derived in terms of this polarisation expression.

Any formulation of nonlinear optics must include a description of the light-matter interactions at a microscopic level. The electromagnetic fields cause the electrons of the material to oscillate (because of the frequencies involved the motions of the heavy ion cores are considered to be of secondary importance). For low field amplitudes the electronic response may be approximated as linear. For higher

amplitudes the nonlinear response of the electrons becomes important (in the language of quantum mechanics, the probability of two or more photons simultaneously incident on the electron becomes significant [5]). In this case the electrons may oscillate at frequencies other than that of the driving fields and thus nonlinear optical phenomena occur. The standard microscopic description of nonlinear optics therefore involves deriving an expression for the material polarisation that is caused by these oscillating electrons.

The microscopic definition of the polarisation density is

$$\mathbf{P}(t) \equiv V^{-1} \langle \boldsymbol{\mu} \rangle, \quad (2.2)$$

where V is a small volume and $\boldsymbol{\mu}$ is the dipole operator. The expectation value is invariably treated using semiclassical theory: the material is treated quantum mechanically and the electromagnetic fields are treated classically. The evaluation of the expectation value (within the electric dipole approximation) gives $\mathbf{P}(t)$ as a function of $\mathbf{E}(t)$, the electric field of the radiation. This is usually carried out using one of two following methods.

At moderate field strengths and in the absence of intermediate resonances $\mathbf{P}(t)$ may be expanded as a power series in $\mathbf{E}(t)$. At each order the material tensor that connects these two variables is found from time-dependent perturbation theory. In the frequency domain these are the usual optical susceptibility tensors. The lowest order susceptibility is $\chi^{(1)}$, which describes linear optics. Higher order tensors describe nonlinear optical phenomena, for example $\chi^{(2)}$ for second-harmonic generation and $\chi^{(3)}$ for four wave mixing. Explicit expressions for these tensors may be found in standard nonlinear optics texts [23, 121].

When very intense light is used or when strong intermediate resonances are present this perturbation-theoretic approach is not valid. A simple but powerful alternative is to employ the two-level model, where many orders of perturbation may be handled together. This is required to describe important dynamical effects such as excited level saturation and Rabi flopping [4].

The fundamental observable in nonlinear optics is the light scattering intensity [87]. In this thesis the scattering intensity is examined in the cases where the input intensities are moderate and strong resonances are absent, i.e. in the cases where a perturbation-theoretic description may be employed. If the first method outlined above is followed, the intensity expression that results is proportional to the squared modulus of the susceptibility tensor appropriate to the process under consideration. This polarisation-based semiclassical optical susceptibility formulation of nonlinear optics is a standard approach. Another, which we adopt here, is to consider the light scattering intensity and associated transition amplitude expressions that are given by the Golden Rule. We follow this fully quantum mechanical alternative because only then are intermediate resonances consistently treated [8] (this issue is discussed in detail in Chap. 6).

2.3 Golden Rule

2.3.1 Basic expression

The Golden Rule expression for the rate of transition, $I^{\{n'_k n_k\}}$, of the electromagnetic field from some initial set of photon occupation numbers $\{n_k\} = n_{k_1}..n_{k_N}$ to some final set $\{n'_k\} = n'_{k_1}..n'_{k_N}$ is

$$I^{\{n'_k n_k\}} = \frac{2\pi}{\hbar} \sum_{\{f\}} \left| V_{\{f\}\{i\}}^{\{n'_k n_k\}} \right|^2 \delta(E_{\{i\}} + E_{\{n_k\}} - E_{\{f\}} - E_{\{n'_k\}}), \quad (2.3)$$

where we have supposed the process under consideration involves N photons, labelled by their modes $\{k\} = k_1..k_N$. The transition rate is mediated by the material system which itself undergoes a transition from an initial state $\{i\}$ to some final state $\{f\}$; all final states not distinguished by measurement are summed over. The Dirac delta function specifies the resonance condition between initial energies $E_{\{i\}}$ and $E_{\{n_k\}}$ and final energies $E_{\{f\}}$ and $E_{\{n'_k\}}$.

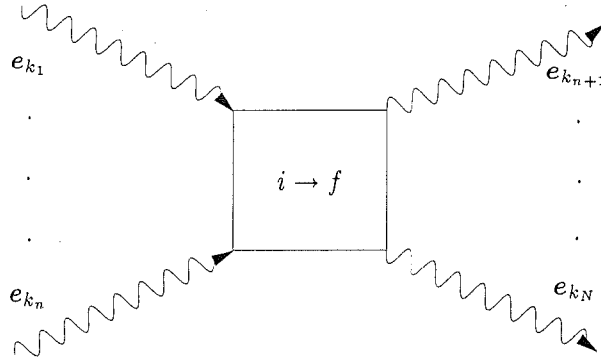


Fig. 2.3: In this thesis we consider the light scattering intensity for the process where the electronic subsystem absorbs photons k_1, \dots, k_n and emits photons k_{n+1}, \dots, k_N .

Equation (2.3) is derived by solving the Schrödinger equation in the interaction picture via a series expansion of the evolution operator in powers of the light-matter interaction Hamiltonian [5, 94, 126]. By assumption, this series rapidly converges and the leading nonzero term suffices to give the transition amplitude $V_{\{f\}\{i\}}^{\{n'_k n_k\}}$ (explicit expressions are given in §2.4.2). This time-dependent perturbation-theoretic approach naturally uses as basis states the eigenstates of the noninteracting radiation and matter Hamiltonians, the former being the number states denoted above. Such states have a totally unspecified phase and a transformation to the coherent state basis is desirable if laser light is to be represented [5]. However, our time reversal results are independent of such basis transformations and we therefore continue use the more convenient number states.

2.3.2 Multi-particle systems

In this thesis we shall consider material systems consisting of M identical particles (e.g. molecules, atoms, electrons). In both the Golden Rule and polarisation-based approaches, the simplifying assumption that these particles are independent is often made. The macroscopic properties may be then related directly to one particle effects. Here we also adopt this assumption so that the amplitude takes the form

$$V_{\{f\}\{i\}}^{\{n'_k n_k\}} = \sum_{m=1}^M V_{\{f\}\{i\};m}^{\{n'_k n_k\}} e^{-i\mathbf{R}_m \cdot \Delta \mathbf{k}}, \quad (2.4)$$

where the sum over m runs over these particles with centres \mathbf{R}_m . The subscript m indicates which centre is interacting; because the particles are independent, two centres cannot together be involved in a given contribution to the amplitude. The wavevector mismatch $\Delta \mathbf{k}$ for the process is $\sum_{p=1}^N \eta_p \mathbf{k}_p$, where \mathbf{k}_p is the wavevector for photon p and η_p is $+1$ if mode k_p involves emission and -1 for absorption.

We shall use Eq.(2.4) to rewrite Eq.(2.3) in terms of one-particle transition amplitudes. We explicitly carry out this simplification because standard treatments appear not to adequately handle degeneracies in the initial and final states. Note, in the following we do not consider the overall motions of the particles with respect to their centre of mass, the only states considered are the electronic energy levels of the particles. Also, we do not explicitly consider any spatial symmetries that may be present as they are independent of our time reversal results (although useful predictions may be obtained when combined with such spatial symmetries, see for example §§3.4 and 6.4).

We first consider the case where the particles are distinguishable (e.g. particles with fixed positions in a lattice). In this case $|\{i\}\rangle = |i_1\rangle \dots |i_M\rangle$, i.e. $|\{i\}\rangle$ may be expressed as a product of one particles states, where each $|i_m\rangle$ is an eigenstate of some one particle unperturbed electronic Hamiltonian; similarly for $|\{f\}\rangle$. Strictly we should include in Eq.(2.3) an average (a weighted sum outside the modulus-squared) over each $|i_m\rangle$ because of the statistical uncertainty in the precise state of particle m . However, if all the particles have the same uncertainty distribution, we may effect this averaging in a simpler manner. In particular, if P_i is the probability that a particle is in the state i we then choose $M_i = P_i M$ particles in $|\{i\}\rangle$ to be in that state; it does not matter which as they are all independent and identical.

In the case where $\{f\} \neq \{i\}$ some particle, say m , must make a transition: $|i_m\rangle \rightarrow |f_m\rangle$. The amplitude then takes the form

$$V_{\{f\} \neq \{i\}}^{\{n'_k n_k\}} = V_{fi}^{\{n'_k n_k\}} e^{-i\mathbf{R}_m \cdot \Delta \mathbf{k}} e^{i(\phi_i^m - \phi_f^m)}, \quad (2.5)$$

where the additional phase factor arises on writing the f_m, i_m in terms of some reference states f, i : $|i_m\rangle = e^{i\phi_i^m} |i\rangle$, $|f_m\rangle = e^{i\phi_f^m} |f\rangle$ [5]. There is no need to include such phases for the photon matrix elements because there is only one fixed set

of modes participating, i.e. they do not vary from particle to particle. The sum over $\{f\}$ in Eq.(2.3) now becomes $\sum_m \sum_{f_m}$. For diagonal transitions, where the electronic system does not change state: $\{f\} = \{i\}$, the situation is different because all M particles now contribute coherently. In particular,

$$V_{\{f\}=\{i\}}^{\{n'_k n_k\}} = \sum_i V_{ii}^{\{n'_k n_k\}} \sum_{n=1}^{M_i} e^{-i\mathbf{R}_n \cdot \Delta \mathbf{k}}, \quad (2.6)$$

where the sum over i includes all states that are populated in $\{i\}$; the extra phases that occurred in Eq.(2.5) cancel for diagonal transitions. The sum on n runs over all particles in state i .

Light scattering processes may be divided into two classes: those that separately conserve the energy of the electronic and photon subsystems (parametric processes) and those that do not (non-parametric processes). The first class may be subdivided into two further classes: those processes which have $\Delta \mathbf{k} = \mathbf{0}$ (coherent processes) and those that do not. Thus, for distinguishable particles the scattering intensity takes one of the following forms

$$I^{\{n'_k n_k\}} = \left| \sum_i M_i V_{ii}^{\{n'_k n_k\}} \right|^2 + \sum_i M_i \sum_{f \neq i} \left| V_{fi}^{\{n'_k n_k\}} \right|^2, \quad (2.7)$$

$$I^{\{n'_k n_k\}} = \left| \sum_i M_i^{1/2} V_{ii}^{\{n'_k n_k\}} \right|^2 + \sum_i M_i \sum_{f \neq i} \left| V_{fi}^{\{n'_k n_k\}} \right|^2, \quad (2.8)$$

$$I^{\{n'_k n_k\}} = \sum_i M_i \sum_f \left| V_{fi}^{\{n'_k n_k\}} \right|^2. \quad (2.9)$$

These three classes represent processes that are coherent, parametric with $\Delta \mathbf{k} \neq \mathbf{0}$, and non-parametric respectively (we have suppressed the resonance condition and constants).

We now consider the case where the particles are indistinguishable (e.g. conduction band electrons) so that the states can only be specified by the occupation numbers M_i . The initial and final electronic states are symmetrised or antisymmetrised for systems of bosons and fermions respectively:

$$|\{i\}\rangle = W_{\{i\}}^{-1/2} \sum_{\pi(1..M)} \zeta_{\pi}^i |i_1\rangle \dots |i_M\rangle \quad |\{f\}\rangle = W_{\{f\}}^{-1/2} \sum_{\pi(1..M)} \zeta_{\pi}^f |f_1\rangle \dots |f_M\rangle, \quad (2.10)$$

where the sums run over all inequivalent permutations of the M states, with the W being the number of such permutations. The ζ_{π} is +1 for symmetrised states and ± 1 for antisymmetrisation. In the case $\{f\} = \{i\}$ the amplitude now takes the form

$$\sum_i V_{ii}^{\{n'_k n_k\}} \sum_{n=1}^{M_i} e^{-i\mathbf{R}_n \cdot \Delta \mathbf{k}} \left(W_{\{i\}}^{-1} \sum_{\pi(1..M)} |\zeta_{\pi}^i|^2 \right), \quad (2.11)$$

and because the term in brackets is unity an identical expression to the unsymmetrised case therefore results. When $\{f\} \neq \{i\}$ a simplification of Eq.(2.4) requires a detailed description of $\{f\}$ and $\{i\}$. This not attempted here. Such a calculation would note that every permutation in $\{i\}$ will lead to a contribution of the form of Eq.(2.5) and that for each such contribution the phases due to the different molecular states are uncorrelated. We shall assume that, at least to within a constant, Eqs.(2.8) and (2.9) are adequate to describe the symmetrised and antisymmetrised cases.

Equations (2.7) to (2.9) reduce to the standard scattering expressions when no degeneracies are present [5]. However, for parametric processes in the case where i, f are degenerate, agreement with the literature is not reached. In particular, we have for diagonal transitions the sum over i inside the modulus-squared whereas Stedman [130] incorrectly places it outside. We explain our form of the diagonal terms by noting that for such transitions one cannot ascertain which particle was involved in the scattering process, and therefore the amplitudes for the various particles are able to interfere, i.e. are summed over. This may be compared with the case of a one particle system with a statistical uncertainty in i , where the sum over i would then be outside the modulus-squared.

An important issue in designing high performance nonlinear optical devices is achieving $\Delta\mathbf{k} = \mathbf{0}$ (wavevector matching) [40]. Because of dispersion, this is a nontrivial problem and in certain cases the best that can be done is to minimise $\Delta\mathbf{k}$. In such intermediate cases, where $e^{-i\mathbf{R}_n \cdot \Delta\mathbf{k}}$ is a slowly varying function of \mathbf{R}_n , the $|\sum_{n=1}^{M_i} e^{-i\mathbf{R}_n \cdot \Delta\mathbf{k}}|^2$ that occurs in Eq.(2.7) gives a M_i^2 dependence that is now modulated by a sinc² function of $\Delta\mathbf{k}$ [5]. However, our later time reversal analyses for coherent processes are independent of the exact form of such multiplicative factors. All we will require is the approximation that the second term of Eq.(2.7) may be neglected in comparison with the first. For simplicity we therefore assume that the required exact wavevector matching may be achieved, and take as the scattering intensity expression for coherent processes

$$I_{\text{coh}}^{\{n'_k n_k\}} = \frac{2\pi}{\hbar} \left| \sum_i M_i V_{ii}^{\{n'_k n_k\}} \right|^2 \delta(E_{\{n_k\}} - E_{\{n'_k\}}). \quad (2.12)$$

Our results for incoherent processes are independent of whether Eqs.(2.8) or (2.9) are used (see Chap. 5). For this reason we shall define

$$I_{\text{incoh}}^{\{n'_k n_k\}} = \frac{2\pi}{\hbar} \sum_i M_i \sum_f \left| V_{fi}^{\{n'_k n_k\}} \right|^2 \delta(E_i + E_{\{n_k\}} - E_f - E_{\{n'_k\}}), \quad (2.13)$$

and leave it as understood that identical results follow for the incoherent parametric case.

Equations (2.12) and (2.13) are the two expression upon which the time reversal analysis of this thesis is based; the focus is thus at the one particle level. Although

all macroscopic effects will ultimately be based on such microscopic interactions, the only macroscopic effect that is directly considered is the scattering intensity. Finally, we shall assume throughout that local field effects may be neglected and that the refractive index may be set to unity. This is strictly valid only for dilute media. However, an index greater than one complicates our notation without affecting our results, and the inclusion of local field effects involves contracting the electronic parts of the amplitude with the local polarisation of the material [5], so that our results may still be usefully applied.

2.4 Notation and explicit expressions

2.4.1 Perturbation term factorisation

The findings of this thesis follow from the application of time reversal to the electronic parts of the scattering intensity. We therefore develop a notation that conveniently describes the factorisation of the transition amplitude into a contraction of principally electronic parts with the photon parts (radiation field amplitudes and polarisation vector components). We do not adopt the notation employed for the optical susceptibility tensors as it too cumbersome for our purposes (see Eq.(2.15)). We instead follow Naguleswaran and Stedman [104, 105] and denote the electronic parts $O_{fi\{k\}}^{\{\alpha,\eta\}}$ and the photon-specific quantities $\gamma_{\{\alpha\}}^{\{n'_k n_k\}}$:

$$V_{fi}^{\{n'_k n_k\}} = \sum_{\{\alpha\}} \gamma_{\{\alpha\}}^{\{n'_k n_k\}} O_{fi\{k\}}^{\{\alpha,\eta\}}. \quad (2.14)$$

The indices $\{\alpha\} = \alpha_1 \dots \alpha_N$ refer to the Cartesian components of the N participating photon polarisation vectors $\{e_k\}$; α_p specifying components of e_{k_p} . All sub- or superscripts associated with photon quantities shall be enclosed by a $\{ \}$, denoting a set of N labels (one for each participating photon). Detailed expressions for the amplitude factors and illustrations of the notation are given in §§2.4.2 and 2.4.3.

For notational compactness we do not factor the photon wavevectors $\{k\}$ into the photon parts. This entails rewriting the magnetic field operator \mathbf{B}_k in terms of the transverse displacement field operator \mathbf{D}_k : $c\mathbf{B}_k = \hat{\mathbf{k}} \times \mathbf{D}_k$ (c is the speed of light), and including this unit wavevector $\hat{\mathbf{k}} = c/\omega_k \mathbf{k}$ in the electronic parts (§2.4.2). For this reason the form of $\gamma_{\{\alpha\}}^{\{n'_k n_k\}}$ is independent of any multipole approximation. For example, the photon-specific parts here are identical to those in Naguleswaran and Stedman [104], where the electric dipole approximation was assumed; although here the radiation field is treated quantum mechanically rather than classically.

The electronic parts contain numerators involving products of matrix elements and denominators involving energy differences. The sign of the photon frequency ω_p appearing in these denominators, and beyond the electric dipole approximation

the sign of the wavevector \mathbf{k}_p in the numerators, differs if photon p is absorbed or emitted. This is labelled by the superscript $\{\eta\} = \eta_1 \dots \eta_N$. Intermediate resonances are included by imaginary parts in each electronic denominator, these have a common sign [8].

In the absence of damping factors, and within the electric dipole approximation (denoted by $\mathbf{0}$), our notation may be compared with that for the optical susceptibility:

$$\sum_i M_i O_{ii\{\mathbf{0}\}}^{\{\alpha, \eta\}} = \chi_{\alpha_N \alpha_1 \dots \alpha_{N-1}}^{(N-1)}(-\eta_N \omega_N; \eta_1 \omega_1, \eta_2 \omega_2, \dots, \eta_{N-1} \omega_{N-1}), \quad (2.15)$$

supposing k_N is the mode of interest and the M_i satisfy a thermal distribution. It will be seen in subsequent chapters that the notation adopted here gives a far more transparent and compact description of time reversal symmetry in light-matter interactions at this and all other multipole levels.

2.4.2 Amplitudes in the multipolar gauge

The electronic parts, $O_{fi\{\mathbf{k}\}}^{\{\alpha, \eta\}}$, of a N photon nonlinear optical transition amplitude take the form:

$$O_{fi\{\mathbf{k}\}}^{\{\alpha, \eta\}} = \sum_{\pi\{\alpha\}, \{s\}} \frac{N_{fi\pi\{\mathbf{k}\}}^{\pi\{\alpha, \eta\}\{s\}}}{D_{fi}^{\pi\{\eta\}\{s\}}} + \mathcal{Q}, \quad (2.16)$$

where

$$N_{fi\{\mathbf{k}\}}^{\{\alpha, \eta\}\{s\}} = \langle f | \xi_{\alpha_N}^{\eta_N, \mathbf{k}_N} | s_{N-1} \rangle \langle s_{N-1} | \xi_{\alpha_{N-1}}^{\eta_{N-1}, \mathbf{k}_{N-1}} | s_{N-2} \rangle \dots \langle s_2 | \xi_{\alpha_2}^{\eta_2, \mathbf{k}_2} | s_1 \rangle \langle s_1 | \xi_{\alpha_1}^{\eta_1, \mathbf{k}_1} | i \rangle, \quad (2.17)$$

$$D_{fi}^{\{\eta\}\{s\}} = (E_{i, s_1} - \hbar \eta_1 \omega_1 + i \Gamma_{s_1}) \dots \left(E_{i, s_{N-1}} - \hbar \sum_{p=1}^{N-1} \eta_p \omega_p + i \Gamma_{s_{N-1}} \right), \quad (2.18)$$

and \mathcal{Q} represents terms involving quadratic interactions. The various possible temporal orderings of the photon interactions are included in the sum over permutations of the polarisation vector components: $\pi\{\alpha\}$. The $N-1$ intermediate electronic state labels $\{s\} = s_1 \dots s_{N-1}$ are summed independently, $E_{i, s} \equiv E_i - E_s$; the finite lifetime of s_j is incorporated into the amplitude via the phenomenological damping factor Γ_{s_j} [8] (the signs associated with these damping factors are justified in Chap. 6). For given index ordering $\{\alpha\}$ in the numerator, the frequency ordering $\{\eta\}$ in the denominator is fixed and hence in Eq.(2.16) the same permutation symbol is used on each; similarly for $\{\mathbf{k}\}$.

In the multipolar gauge the nonrelativistic parts of the light-matter interaction Hamiltonian, H_{int} , take the form [33]

$$-\varepsilon_0^{-1} \int d^3 r \mathbf{D} \cdot \mathbf{P} - \int d^3 r \mathbf{M} \cdot \mathbf{B}, \quad (2.19)$$

where the electric polarisation \mathbf{P} and magnetisation \mathbf{M} are

$$\mathbf{P}(\mathbf{r}) = \sum_{\beta} \int_0^1 du q_{\beta} \mathbf{r}_{\beta} \delta(\mathbf{r} - u \mathbf{r}_{\beta}), \quad (2.20)$$

$$\mathbf{M}(\mathbf{r}) = \sum_{\beta} \int_0^1 u du q_{\beta} \mathbf{r}_{\beta} \times \dot{\mathbf{r}}_{\beta} \delta(\mathbf{r} - u \mathbf{r}_{\beta}), \quad (2.21)$$

respectively. The position of particle β , with charge q_{β} and mass m_{β} , within the scatterer is denoted \mathbf{r}_{β} ; \mathbf{p}_{β} is the corresponding conjugate momentum operator. For reasons described below we include in H_{int} additional light-matter couplings that arise from the inclusion of the spin-orbit interaction in a gauge invariant manner. We denote by ξ the electronic parts of H_{int} (with photon wavevectors included). The $\xi_{\alpha}^{\eta, \mathbf{k}}$ in Eq.(2.17) corresponds to the Cartesian components of the linear parts of ξ associated with $(\mathbf{e}_k)_{\alpha}$:

$$\begin{aligned} \xi_{\alpha}^{\eta, \mathbf{k}} = & \sum_{\beta} - \int_0^1 du q_{\beta} \left\{ \left(e^{-i u \eta \mathbf{k} \cdot \mathbf{r}_{\beta}} \mathbf{r}_{\beta} \right. \right. \\ & + \frac{u}{2 m_{\beta} c} \left((\mathbf{r}_{\beta} \times \mathbf{p}_{\beta}) e^{-i u \eta \mathbf{k} \cdot \mathbf{r}_{\beta}} + e^{-i u \eta \mathbf{k} \cdot \mathbf{r}_{\beta}} (\mathbf{r}_{\beta} \times \mathbf{p}_{\beta}) \right) \times \hat{\mathbf{k}} \Big)_{\alpha} \\ & \left. - \frac{q_{\beta} u}{2 m_{\beta} c^3} e^{-i u \eta \mathbf{k} \cdot \mathbf{r}_{\beta}} \left(\hat{\mathbf{k}} \cdot \mathbf{r}_{\beta} (\mathbf{s}_{\beta} \times \mathbf{E}_C(\mathbf{r}_{\beta}))_{\alpha} - (\mathbf{s}_{\beta} \times \mathbf{E}_C(\mathbf{r}_{\beta})) \cdot \hat{\mathbf{k}} (\mathbf{r}_{\beta})_{\alpha} \right) \right\}, \end{aligned} \quad (2.22)$$

where the term on first line arises from the $\mathbf{D} \cdot \mathbf{P}$ and the terms on the second line from the linear parts of the $\mathbf{M} \cdot \mathbf{B}$, the term on the last line is associated with the relativistic correction of spin-orbit coupling (as discussed below); \mathbf{E}_C is the Coulombic part of the electric field:

$$\mathbf{E}_C(\mathbf{r}) = \frac{1}{4\pi\epsilon_0} \sum_{\beta} q_{\beta} \frac{\mathbf{r} - \mathbf{r}_{\beta}}{|\mathbf{r} - \mathbf{r}_{\beta}|^3}. \quad (2.23)$$

The quadratic part of ξ , which arises from the diamagnetic interaction associated with Eq.(2.21), is

$$\begin{aligned} \xi_{\alpha\alpha'}^{\eta\eta', \mathbf{k}\mathbf{k}'} = & \sum_{\beta} \frac{q_{\beta}^2}{2 m_{\beta} c^2} \int_0^1 u du \int_0^1 u' du' e^{-i(u\eta\mathbf{k} + u'\eta'\mathbf{k}') \cdot \mathbf{r}_{\beta}} \left(\mathbf{r}_{\beta}^2 \hat{\mathbf{k}} \cdot \hat{\mathbf{k}}' \delta_{\alpha\alpha'} \right. \\ & \left. - \mathbf{r}_{\beta}^2 (\hat{\mathbf{k}}')_{\alpha} (\hat{\mathbf{k}})_{\alpha'} - (\mathbf{r}_{\beta} \times \hat{\mathbf{k}})_{\alpha} (\mathbf{r}_{\beta} \times \hat{\mathbf{k}}')_{\alpha'} \right), \end{aligned} \quad (2.24)$$

which is invariant under the interchange of primed and unprimed labels because such an interchange gives an identical temporal ordering of photon interactions. The terms in \mathcal{Q} , which involve at least one matrix element of $\xi_{\alpha\alpha'}$, are of a similar form as the linear terms in Eq.(2.16), but with necessarily fewer intermediate interactions. These quadratic terms introduce no new points of interest over the linear terms, and for notational convenience are suppressed. We leave it as understood that our derivations apply equally well to \mathcal{Q} (see §3.1.5 for an example). Incidentally, there are no quadratic terms in the electric dipole approximation,

and Kobe and Yang [77] show that even those dipole terms that exist in the Coulomb gauge (Eq.(2.47)) cancel. (However, care must be taken when considering lowest order contributions to Rayleigh scattering where such terms must in fact be included [3].)

Equation (10) of Wang and Stedman [137] gives the Coulomb gauge expression for the spin-orbit term plus the associated light-matter interaction terms:

$$\sum_{\beta} \frac{q_{\beta}}{4m_{\beta}c^2} \mathbf{s}_{\beta} \cdot ((\mathbf{p}_{\beta} - q_{\beta}\mathbf{A}(\mathbf{r}_{\beta})) \times \mathbf{E}_C - \mathbf{E}_C \times (\mathbf{p}_{\beta} - q_{\beta}\mathbf{A}(\mathbf{r}_{\beta}))), \quad (2.25)$$

where \mathbf{A} is the transverse vector potential operator. Wang and Stedman [137] obtain this and other relativistic corrections by the usual Foldy-Wouthuysen-Tani transformation of the Dirac equation into the Schrödinger-Pauli equation. As discussed in §3.1.1, all such relativistic corrections may be readily incorporated into our analysis. We have included in Eq.(2.22) the spin-orbit term because certain of our selection rules are nontrivial only when this is done (§4.3.2). The transformation of Eq.(2.25) to the multipolar gauge is effected by a unitary operator F (see §2.5)

$$F = \exp \frac{i}{\hbar} \int d^3r \mathbf{P}(\mathbf{r}) \cdot \mathbf{A}(\mathbf{r}), \quad (2.26)$$

$$F^{\dagger} (\text{Eq.}(2.25)) F = - \sum_{\beta} \frac{q_{\beta}}{2m_{\beta}c^2} \mathbf{s}_{\beta} \cdot \mathbf{E}_C \times \left(\mathbf{p}_{\beta} - q_{\beta} \int_0^1 du u \mathbf{B}(\mathbf{r}_{\beta}u) \times \mathbf{r}_{\beta} \right). \quad (2.27)$$

The first term of Eq.(2.27) gives the usual spin-orbit term which is included in the unperturbed electronic Hamiltonian, and the second term gives the last term of Eq.(2.22). Separately these two terms are not form invariant under a gauge transformation, and only together do they correspond to an observable (see Eq.(2.48)). We take particular care over such distinctions because in this thesis we consider the gauge invariance of our results (§4.4).

Finally, the photon parts of the amplitude, which involve N matrix elements of the displacement operator (Eq.(3.15)), take the form

$$\gamma_{\{\alpha\}}^{\{n'_k n_k\}} = \prod_{i=1}^N K_i, \quad (2.28)$$

where for mode k_i involving absorption

$$K_i = i\phi_1 c_{k_i} \langle n_{k_i} - 1 | a_{k_i} | n_{k_i} \rangle (\mathbf{e}_{k_i})_{\alpha_i}, \quad (2.29)$$

and for emission

$$K_i = -i\phi_1^* c_{k_i}^{\dagger} \langle n_{k_i} + 1 | a_{k_i}^{\dagger} | n_{k_i} \rangle (\mathbf{e}_{k_i}^*)_{\alpha_i}; \quad (2.30)$$

these expressions are valid for the terms in \mathcal{Q} also. The phase ϕ_1 is discussed in §3.1.2, a_k and a_k^{\dagger} are annihilation and creation operators for mode k , and $c_k = \sqrt{\hbar\omega_k/2\varepsilon_0 L^3}$, with L^3 being the quantisation volume.

2.4.3 Examples

We give two examples to illustrate this notation. The first example regards the amplitude for Rayleigh scattering from electronic state i to f and in which a photon from mode k_1 is absorbed, and a photon from mode k_2 is emitted. In this case Eq.(2.14) is

$$\gamma_{\{\alpha\}}^{\{n'_k n_k\}} \Big|_{\text{RS}} = c_{k_1} c_{k_2} \langle n_{k_1} - 1 | a_{k_1} | n_{k_1} \rangle \langle n_{k_2} + 1 | a_{k_2}^\dagger | n_{k_2} \rangle (e_{k_1})_{\alpha_1} (e_{k_2}^*)_{\alpha_2}, \quad (2.31)$$

$$O_{fi\{k\}}^{\{\alpha, \eta\}} \Big|_{\text{RS}} = \sum_{s_1} \frac{\langle f | \xi_{\alpha_2}^{+, k_2} | s_1 \rangle \langle s_1 | \xi_{\alpha_1}^{-, k_1} | i \rangle}{E_{i, s_1} + \hbar\omega_1 + i\Gamma_{s_1}} + \frac{\langle f | \xi_{\alpha_1}^{-, k_1} | s_1 \rangle \langle s_1 | \xi_{\alpha_2}^{+, k_2} | i \rangle}{E_{i, s_1} - \hbar\omega_1 + i\Gamma_{s_1}}. \quad (2.32)$$

The two terms correspond to the cases in which photon 1 is first absorbed and in which photon 2 is first emitted (see Fig. 2.4). The various $N_{fi\{k\}}^{\{\alpha, \eta\}\{s\}}$ and $D_{fi}^{\{\eta\}\{s\}}$ can be read off the two terms in Eq.(2.32) as

$$N_{fi\mathbf{k}_1\mathbf{k}_2}^{\alpha_1\alpha_2, \eta_1\eta_2, s_1} = \langle f | \xi_{\alpha_2}^{+, k_2} | s_1 \rangle \langle s_1 | \xi_{\alpha_1}^{-, k_1} | i \rangle, \quad (2.33)$$

$$N_{fi\mathbf{k}_2\mathbf{k}_1}^{\alpha_2\alpha_1, \eta_2\eta_1, s_1} = \langle f | \xi_{\alpha_1}^{-, k_1} | s_1 \rangle \langle s_1 | \xi_{\alpha_2}^{+, k_2} | i \rangle, \quad (2.34)$$

$$D_{fi}^{\eta_1\eta_2, s_1} = E_{i, s_1} + \hbar\omega_1 + i\Gamma_{s_1}, \quad (2.35)$$

$$D_{fi}^{\eta_2\eta_1, s_1} = E_{i, s_1} - \hbar\omega_1 + i\Gamma_{s_1}. \quad (2.36)$$

The expression for the total amplitude is

$$V_{fi}^{\{n'_k n_k\}} \Big|_{\text{RS}} = c_{k_1} c_{k_2} \langle n_{k_1} - 1 | a_{k_1} | n_{k_1} \rangle \langle n_{k_2} + 1 | a_{k_2}^\dagger | n_{k_2} \rangle \times \\ \left(\sum_{s_1} \frac{\langle f | e_{k_2}^* \cdot \xi^{+, k_2} | s_1 \rangle \langle s_1 | e_{k_1} \cdot \xi^{-, k_1} | i \rangle}{E_{i, s_1} + \hbar\omega_1 + i\Gamma_{s_1}} + \frac{\langle f | e_{k_1} \cdot \xi^{-, k_1} | s_1 \rangle \langle s_1 | e_{k_2}^* \cdot \xi^{+, k_2} | i \rangle}{E_{i, s_1} - \hbar\omega_1 + i\Gamma_{s_1}} \right) \quad (2.37)$$

in this example.

Another example is that of second-harmonic generation. If two photons of frequency ω_1 and polarisation e_{k_1} are absorbed, and one of doubled frequency $\omega_3 = 2\omega_1$ and polarisation e_{k_3} is emitted, the relevant amplitude factors have the form $\gamma_{\{\alpha\}}^{\{n'_k n_k\}}|_{\text{SHG}} = i\phi_1 c_{k_1}^2 c_{k_3} \times$

$$\langle n_{k_1} - 2 | a_{k_1} | n_{k_1} - 1 \rangle \langle n_{k_1} - 1 | a_{k_1} | n_{k_1} \rangle \langle n_{k_3} + 1 | a_{k_3}^\dagger | n_{k_3} \rangle (e_{k_1})_{\alpha_1} (e_{k_1})_{\alpha_2} (e_{k_3}^*)_{\alpha_3}, \quad (2.38)$$

$$O_{fi\{k\}}^{\{\alpha, \eta\}} \Big|_{\text{SHG}} = \sum_{s_1, s_2} \frac{\langle f | \xi_{\alpha_3}^{+, k_3} | s_2 \rangle \langle s_2 | \xi_{\alpha_2}^{-, k_1} | s_1 \rangle \langle s_1 | \xi_{\alpha_1}^{-, k_1} | i \rangle}{(E_{i, s_1} + \hbar\omega_1 + i\Gamma_{s_1}) (E_{i, s_2} + 2\hbar\omega_1 + i\Gamma_{s_2})} \\ + \frac{\langle f | \xi_{\alpha_2}^{-, k_1} | s_2 \rangle \langle s_2 | \xi_{\alpha_3}^{+, k_3} | s_1 \rangle \langle s_1 | \xi_{\alpha_1}^{-, k_1} | i \rangle}{(E_{i, s_1} + \hbar\omega_1 + i\Gamma_{s_1}) (E_{i, s_2} + \hbar\omega_1 - \hbar\omega_3 + i\Gamma_{s_2})} \\ + \frac{\langle f | \xi_{\alpha_1}^{-, k_1} | s_2 \rangle \langle s_2 | \xi_{\alpha_2}^{-, k_1} | s_1 \rangle \langle s_1 | \xi_{\alpha_3}^{+, k_3} | i \rangle}{(E_{i, s_1} - \hbar\omega_3 + i\Gamma_{s_1}) (E_{i, s_2} - \hbar\omega_3 + \hbar\omega_1 + i\Gamma_{s_2})}, \quad (2.39)$$

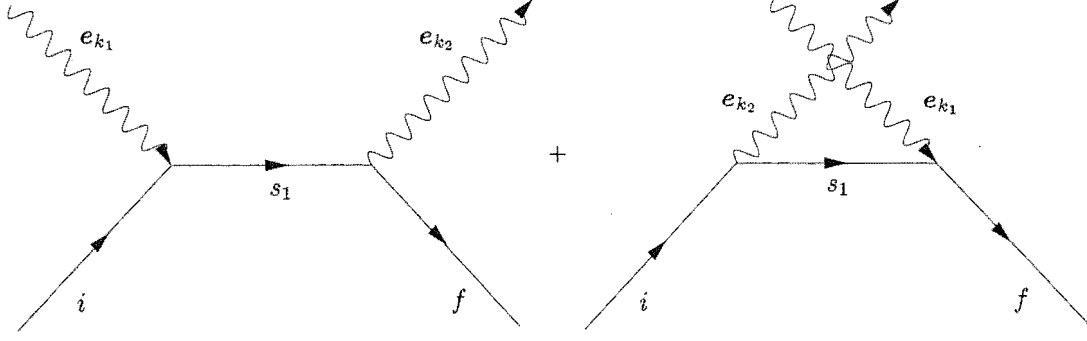


Fig. 2.4: The lowest order contribution to Rayleigh scattering may be represented diagrammatically as shown. The two diagrams correspond to the two terms in Eq.(2.37) when damping factors may be neglected.

where the three terms correspond to each of the three inequivalent permutations of the photon labels 1, 2, 3 (see Fig. 2.5). For example, the second term has $\pi(2) = 3$ $\pi(3) = 2$, corresponding to the temporal ordering 1 absorbed, 3 emitted, 2 absorbed has the numerator and denominator:

$$N_{fi k_1 k_3 k_2}^{\alpha_1 \alpha_3 \alpha_2, s_1 s_2} = \langle f | \xi_{\alpha_2}^{-, k_1} | s_2 \rangle \langle s_2 | \xi_{\alpha_3}^{+, k_3} | s_1 \rangle \langle s_1 | \xi_{\alpha_1}^{-, k_1} | i \rangle, \quad (2.40)$$

$$D_{fi}^{\eta_1 \eta_3 \eta_2, s_1 s_2} = (E_{i, s_1} + \hbar \omega_1 + i \Gamma_{s_1}) (E_{i, s_2} + \hbar \omega_1 - \hbar \omega_3 + i \Gamma_{s_2}). \quad (2.41)$$

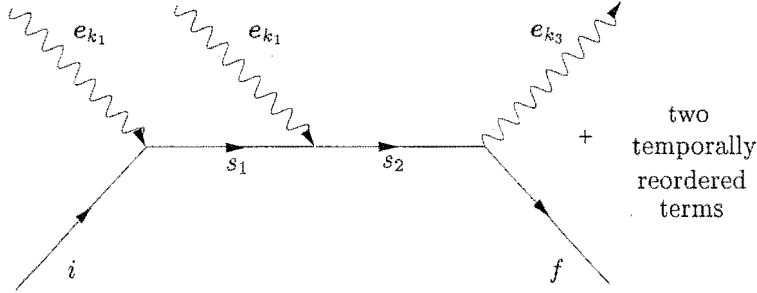


Fig. 2.5: The diagrammatic representation of the lowest order contribution to second-harmonic generation involves three terms corresponding to the three inequivalent temporal orderings of the photon interactions. The ordering shown is for 1 absorbed, 2 absorbed, 3 emitted given by the first term in Eq.(2.39).

2.5 Coulomb gauge

2.5.1 Transformation between gauges

The interaction of nonrelativistic charges with electromagnetic fields is most conveniently expressed in the multipolar gauge. However, when damping factors

may be ignored (see below), certain calculations are also usefully carried out in the Coulomb gauge. For this reason we shall verify that in the nonresonant limit identical time reversal results are obtained for both gauge choices. This verification is nontrivial (see Chap. 4). In preparation for this, we discuss here the transformation between, and the equivalence of, the amplitudes found in either gauge. This relies upon the results of the well established, but not widely known, gauge invariant formulation of quantum mechanics; the key results of which are summarised below. For a full and excellent discussion of this theory see Cohen-Tannoudji *et al.* [33, 32].

As previously mentioned, the only restriction we have placed on the unperturbed electronic Hamiltonian is that it is time-even. However, for the purposes of discussing gauge invariance, and for only this purpose, we must specify its form (in the multipolar gauge) as

$$H_{\text{elec}} = \sum_{\beta} \left(\frac{\mathbf{p}_{\beta}^2}{2m_{\beta}} - \frac{q_{\beta}}{2m_{\beta}c^2} \mathbf{s}_{\beta} \cdot \mathbf{E}_C \times \mathbf{p}_{\beta} \right) + V_{\text{Coul}} + \int d^3k \varepsilon_0^{-1} |P_{\perp}|^2. \quad (2.42)$$

We have assumed the system of localised charges making up the particle are sufficiently near to one another that in addition to the spin-orbit interaction discussed in §2.4.2 the Coulomb interaction, V_{Coul} , is a very good approximation to their real interaction:

$$V_{\text{Coul}} = \sum_{\beta' > \beta} \frac{q_{\beta'} q_{\beta}}{4\pi\varepsilon_0 |\mathbf{r}_{\beta'} - \mathbf{r}_{\beta}|} + \sum_{\beta} \varepsilon_{\text{Coul}}^{\beta}, \quad (2.43)$$

where $\varepsilon_{\text{Coul}}^{\beta}$ is the Coulomb self energy of particle β . The final term in H_{elec} is a field-independent contribution from the transverse electrical polarisation, which is of importance in calculations such as the Lamb shift [58]; this does not appear in the semiclassical formalism [12]. The unperturbed radiation Hamiltonian is

$$H_{\text{rad}} = \sum_k \left(a_k^{\dagger} a_k + \frac{1}{2} \right) \hbar \omega_k. \quad (2.44)$$

The interaction Hamiltonian has been given in Eqs.(2.22) and (2.24).

General gauge transformations in quantum mechanics are effected by a unitary operator F ; its specific form in going between the multipolar and Coulomb gauges has been given in Eq.(2.26). Under this transformation we have ($H_{\text{multipolar}} = H_{\text{elec}} + H_{\text{rad}} + H_{\text{int}}$)

$$H_{\text{Coulomb}} = F H_{\text{multipolar}} F^{\dagger}, \quad (2.45)$$

where the unperturbed parts of H_{Coulomb} are identical to Eqs.(2.42) and (2.44), although the transverse polarisation is now absent, and the interaction Hamiltonian now takes the form

$$\xi_{\alpha; \text{Coul}}^{\eta, \mathbf{k}} = \sum_{\beta} -\frac{q_{\beta}}{m_{\beta}} e^{-i\eta \mathbf{k} \cdot \mathbf{r}_{\beta}} (\mathbf{p}_{\beta})_{\alpha} + \frac{q_{\beta}^2}{2m_{\beta}c^2} e^{-i\eta \mathbf{k} \cdot \mathbf{r}_{\beta}} (\mathbf{s}_{\beta} \times \mathbf{E}_C(\mathbf{r}_{\beta}))_{\alpha}, \quad (2.46)$$

$$\xi_{\alpha\alpha'; \text{Coul}}^{\eta\eta', \mathbf{k}\mathbf{k}'} = \sum_{\beta} \frac{q_{\beta}^2}{2m_{\beta}} e^{-i(\eta\mathbf{k} + \eta'\mathbf{k}') \cdot \mathbf{r}_{\beta}} \delta_{\alpha\alpha'}. \quad (2.47)$$

The first term of Eq.(2.46) and Eq.(2.47) are the electronic parts of the usual $\mathbf{A} \cdot \mathbf{p}$ and \mathbf{A}^2 interactions respectively; the second term of Eq.(2.46) is associated with spin-orbit coupling, as given in Eq.(2.25).

The evolution operator $U(t, t_0)$ (under which the state vector, ψ , transforms as $|\psi(t)\rangle = U(t, t_0) |\psi(t_0)\rangle$) satisfies $U'(t, t_0) = FU(t, t_0)F^\dagger$, where the prime indicates some arbitrary new gauge. States φ transform as $|\varphi\rangle \rightarrow |\varphi'\rangle = F|\varphi\rangle$, so that the transition amplitude $\langle\varphi|U(t, t_0)|\psi(t_0)\rangle$ is gauge invariant. Physical observables \mathcal{O}_{ob} such as the position \mathbf{r}_β , the kinetic momentum $\boldsymbol{\pi}_\beta \equiv m_\beta \dot{\mathbf{r}}_\beta = \mathbf{p}_\beta - q\mathbf{A}(\mathbf{r}_\beta)$ and the Hamiltonian satisfy

$$\mathcal{O}'_{\text{ob}} = F\mathcal{O}_{\text{ob}}F^\dagger, \quad (2.48)$$

because their mean values are independent of F , as required for an observable. These properties, along with

$$i\hbar \frac{\partial}{\partial t} \psi = H\psi \rightarrow i\hbar \frac{\partial}{\partial t} \psi' = H'\psi', \quad (2.49)$$

guarantee the gauge invariance of the theory. Note that operators which transform differently to \mathcal{O}_{ob} do not correspond to observables. These include H_{elec} , H_{rad} , H_{int} , the full Hamiltonian in the external field (time-dependent) case, and the canonical momentum $\mathbf{p} = -i\hbar\nabla$. This last example follows because \mathbf{p}' is assigned $-i\hbar\nabla$ in the canonical quantisation procedure even though $-i\hbar F\nabla F^\dagger \neq -i\hbar\nabla$.

We have defined our initial and final electronic+photon states in terms of the unperturbed Hamiltonians ($H_{\text{elec}} + H_{\text{rad}}$). In contrast to the external field case in the electric dipole approximation (Yang [141]), we cannot choose a gauge where this noninteracting light-matter Hamiltonian corresponds to some physically useful quantity. To give a gauge-invariant definition of the initial and final light-matter states we must use the full light-matter Hamiltonian and any other definition, such as the one used here, involves some approximation [33].

A question that received much attention in the early '80s is: when can we safely ignore the rephasing of the basis functions that the formalism requires ($|\varphi'\rangle = F|\varphi\rangle$), and so when in the Coulomb gauge can we use the same initial and final kets as in the multipolar gauge? Such instances include transition rates when no intermediate resonances are present. Aharonov and Au [2] show this generally (they do not even assume an Abelian gauge theory). In §2.5.2 we summarise and extend the discussion of Lee and Albrecht [84], who are specifically concerned with electromagnetism. Lee and Albrecht [84] conclude that in the absence of damping factors, the Coulomb gauge amplitude may be found from the multipolar gauge amplitude by a simple replacement of interaction Hamiltonians: $\xi \rightarrow \xi_{\text{Coul}}$ (in Eq.(2.16)). Our extension involves removing the electric dipole approximation, using a quantised radiation field and including the spin-orbit interaction.

For nonzero damping factors this replacement of interaction Hamiltonians no longer gives equivalent amplitudes [84], and the full machinery involved in the

gauge invariant formulation of quantum mechanics must be employed to obtain equivalent expressions [33] (see also Lamb *et al.* [80]). Such a calculation is not attempted here. For this reason, if damping is to be considered we employ the multipolar gauge expression. The Coulomb gauge expression is specifically referred to in §4.4 when considering the gauge invariance of selection rules found in the nonresonant limit (where damping factors may be ignored).

2.5.2 Equivalence of transition amplitudes

Here we follow Lee and Albrecht [84] in showing that in the absence of intermediate resonances the lowest order contributions to overall resonant transition probabilities and rates are unaffected by choosing the initial and final states to be eigenstates of $(H_{\text{elec}} + H_{\text{rad}})$ in the Coulomb gauge.

The proof involves examining the one particle amplitude

$$\langle \{n'_k\} | \langle f | U(t, t_0) | i \rangle | \{n_k\} \rangle, \quad (2.50)$$

when the evolution operator is evaluated in the multipolar and Coulomb gauges; for these two cases Eq.(2.50) is denoted a_f and a'_f respectively. Let $|\nu\rangle$ denote an eigenstate of the unperturbed Hamiltonian $(H_{\text{elec}} + H_{\text{rad}})$. Then, because $|\psi'(t)\rangle = F|\psi(t)\rangle$,

$$\begin{aligned} \sum_{\tilde{\nu}} |\tilde{\nu}\rangle \langle \tilde{\nu} | \psi'(t) \rangle &= \sum_{\nu, \tilde{\nu}} |\tilde{\nu}\rangle \langle \tilde{\nu} | F | \nu \rangle \langle \nu | \psi(t) \rangle, \\ a'_f(t) &= \sum_{\nu} \langle \{n'_k\} | \langle f | F | \nu \rangle a_{\nu}(t). \end{aligned} \quad (2.51)$$

We now expand $a_f(t)$ and $a'_f(t)$ as power series in the field strength, i.e. $a_f(t) = \sum_{s=0}^{\infty} a_f^{(s)}(t)$. Now, using $F = \sum_{s=0}^{\infty} Y^s/s!$ with $Y = i \int d^3r \mathbf{P}(\mathbf{r}) \cdot \mathbf{A}(\mathbf{r})/\hbar$, we have

$$a'_f(t) = \sum_{\nu} \sum_{u=0}^N \frac{1}{u!} \langle \{n'_k\} | \langle f | Y^u | \nu \rangle a_{\nu}^{(N-u)}(t); \quad (2.52)$$

$$R_f \equiv a_f^{(N)'}(t) - a_f^{(N)}(t) \quad (2.53)$$

$$= \sum_{\nu} \sum_{u=1}^N \frac{1}{u!} \langle \{n'_k\} | \langle f | Y^u | \nu \rangle a_{\nu}^{(N-u)}(t). \quad (2.54)$$

Since $(N - u) < N$, and assuming there are no intermediate resonances, R_f is finite.

Let us find the amplitudes $a_f^{(N)}(t)$ and $a_f^{(N)'}(t)$ using adiabatic switching, where the interaction Hamiltonian is multiplied by $e^{\varepsilon t}$ and $\varepsilon \rightarrow 0^+$ at the end of the calculation [94]. Integrating the Schödinger equation gives

$$U_I(t, t_0) = 1 - \frac{i}{\hbar} \int_{t_0}^t H_{\text{int}}^I(t_1) U_I(t_1, t_0) dt_1, \quad (2.55)$$

where the label I indicates the interaction picture. On iteration, this gives the Dyson series $U_I(t, t_0) = \sum_{n=0}^{\infty} U_I^{(n)}(t, t_0)$ where

$$U_I^{(n)}(t, t_0) = \left(\frac{-i}{\hbar}\right)^n \int_{t_0}^t \int_{t_0}^{t_n} \dots \int_{t_0}^{t_2} dt_n dt_{n-1} \dots dt_1 H_{\text{int}}^I(t_n) H_{\text{int}}^I(t_{n-1}) \dots H_{\text{int}}^I(t_1). \quad (2.56)$$

On forming $\langle \{n'_k\}_I | \langle f_I | U_I(t, t_0) | i_I \rangle | \{n_k\}_I \rangle$ and evaluating the time integrals we have

$$a_f^{(N)'}(t) = \frac{V_{fi}^{\{n'_k n_k\}'} e^{-i(E_{\{n_k\}} + E_i)t/\hbar} e^{N\varepsilon t}}{E_i - E_f + E_{\{n_k\}} - E_{\{n'_k\}} + i\hbar N\varepsilon}, \quad (2.57)$$

$$a_f^{(N)}(t) = \frac{V_{fi}^{\{n'_k n_k\}} e^{-i(E_{\{n_k\}} + E_i)t/\hbar} e^{N\varepsilon t}}{E_i - E_f + E_{\{n_k\}} - E_{\{n'_k\}} + i\hbar N\varepsilon}, \quad (2.58)$$

where $V_{fi}^{\{n'_k n_k\}'}$ differs from $V_{fi}^{\{n'_k n_k\}}$ by the replacement of interaction Hamiltonians: $\xi \rightarrow \xi_{\text{Coul}}$. The N arises in the denominator because of the N factors of the interaction Hamiltonian and so of $e^{\varepsilon t}$ [94]. We now suppose we have overall resonance, i.e. $E_i - E_f = E_{\{n'_k\}} - E_{\{n_k\}}$. From Eq.(2.53)

$$R_f = \frac{\left(V_{fi}^{\{n'_k n_k\}'} - V_{fi}^{\{n'_k n_k\}} \right) e^{-i(E_{\{n_k\}} + E_i)t/\hbar} e^{N\varepsilon t}}{i\hbar N\varepsilon}, \quad (2.59)$$

so as $\varepsilon \rightarrow 0$, $R_f \propto \varepsilon^{-1}$. However, by Eq.(2.54) R_f is finite for all ε , hence at resonance we must have

$$V_{fi}^{\{n'_k n_k\}'} = V_{fi}^{\{n'_k n_k\}}, \quad (2.60)$$

i.e. if there are no intermediate resonances, overall resonant transition rates are equivalent in the two gauges without the need for rephasing.

Grynberg and Giacobino [51] give explicit verifications of Eq.(2.60) for the lowest few orders in the electric dipole approximation using the velocity-position relation

$$\langle f | \frac{p^\alpha}{m} | i \rangle = \frac{i}{\hbar} E_{f,i} \langle f | r^\alpha | i \rangle; \quad (2.61)$$

Eq.(2.61) follows directly from Eq.(2.42) when the spin-orbit term is ignored. We have elsewhere (private notes) carried out such a verification up to and including $N=3$. Craig and Thirunamachandran [35] also prove Eq.(2.61) for the lowest few orders, but neither assumes the velocity-position relation nor makes explicit use of the adiabatic switching procedure.

3. Reversality theorems and Onsager relations

We combine the ideas of the previous chapter to give the relations that follow from the application of time reversal symmetry to a general nonlinear optical process (§3.1). As a first application of these relations we derive nonlinear optical Onsager relations for a restricted class of coherent processes (§§3.2 and 3.3). This analysis also allows us to correct the linear optical Onsager relations of Bungay *et al.* [22] (§3.4).

3.1 Reversality theorems

In Chap. 2 we introduced the concept of time reversal (§2.1) and gave the Golden Rule expression for the scattering intensity of a general nonlinear optical process (§§2.3 and 2.4). In this section we apply the former symmetry to the later physical situation. In particular, we examine the action of hermitian conjugation H , time reversal T , and their combination HT on the transition amplitude. The three relations that follow are central to the results of this thesis. As described below, these relations have been known for some time. Our extension is to include the phenomenological damping factors Γ in the energy denominator parts of the transition amplitude. This generalisation is crucial since in later sections and chapters we wish to consider nonlinear optical processes which involve intermediate resonances.

3.1.1 Electronic symmetries

Consider the matrix element $\langle f|\mathcal{O}|i\rangle$ of an arbitrary operator \mathcal{O} . The application of H , T and HT gives

$$(\langle i|\mathcal{O}^\dagger|f\rangle)^* \quad (\langle \bar{f}|\bar{\mathcal{O}}|\bar{i}\rangle)^* \quad \langle \bar{i}|\bar{\mathcal{O}}^\dagger|\bar{f}\rangle \quad (3.1)$$

respectively [130], where H is designated by a superscript dagger and T by an overbar:

$$\mathbf{T}\mathcal{O}\mathbf{T}^{-1} = \bar{\mathcal{O}} \quad \mathbf{T}|i\rangle = |\bar{i}\rangle. \quad (3.2)$$

The complex conjugation in Eq.(3.1) reflects the antilinear nature of the H and T operations.

To illustrate the derivation of these three symmetries on the electronic parts of the transition amplitude we first consider their separate application to the numerator and the denominator parts of $O_{fi\{\mathbf{k}\}}^{\{\alpha,\eta\}}$ (Eq.(2.16)). In the case where $\mathcal{O} = \xi_{\alpha}^{\eta,\mathbf{k}}$, the electronic parts of the interaction Hamiltonian (Eq.(2.22)), we have

$$(\xi_{\alpha}^{\eta,\mathbf{k}})^{\dagger} = \xi_{\alpha}^{-\eta,\mathbf{k}} \quad (\overline{\xi_{\alpha}^{\eta,\mathbf{k}}}) = \xi_{\alpha}^{\eta,-\mathbf{k}} \quad (\overline{\xi_{\alpha}^{\eta,\mathbf{k}}})^{\dagger} = \xi_{\alpha}^{-\eta,-\mathbf{k}}, \quad (3.3)$$

which follows directly from the form of the time reversal operator T (Eq.(2.1)). These symmetries either convert an absorption matrix element into an emission matrix element or vice versa (H), reverse the direction of the photon wavevector (T), or both (HT). It is expected that if relativistic corrections to the light-matter Hamiltonian are included [137], $\xi_{\alpha}^{\eta,\mathbf{k}}$ will continue to satisfy these relations, and therefore our analysis needs no modifications to allow for such incorporations. Equation (3.3) explicitly verifies that the spin-orbit term and associated interactions terms (Eq.(2.27)) are readily included.

By Eq.(3.3) the numerator of $O_{fi\{\mathbf{k}\}}^{\{\alpha,\eta\}}$ (Eq.(2.17)) transforms under H, T and HT as

$$\begin{aligned} N_{fi\{\mathbf{k}\}}^{\{\alpha,\eta\}\{s\}} &= \left(\langle i | \xi_{\alpha_1}^{-\eta_1, \mathbf{k}_1} | s_1 \rangle \dots \langle s_{N-1} | \xi_{\alpha_N}^{-\eta_N, \mathbf{k}_N} | f \rangle \right)^* \\ &= \left(N_{if\{r\}\{\mathbf{k}\}}^{r\{\alpha, -\eta\}\{\rho(s)\}} \right)^*, \end{aligned} \quad (3.4)$$

$$\begin{aligned} N_{fi\{\mathbf{k}\}}^{\{\alpha,\eta\}\{s\}} &= \left(\langle \bar{f} | \xi_{\alpha_N}^{\eta_N, -\mathbf{k}_N} | \bar{s}_{N-1} \rangle \dots \langle \bar{s}_1 | \xi_{\alpha_1}^{\eta_1, -\mathbf{k}_1} | \bar{i} \rangle \right)^* \\ &= \left(N_{\bar{f}\bar{i}\{-\mathbf{k}\}}^{\{\alpha,\eta\}\{\bar{s}\}} \right)^*, \end{aligned} \quad (3.5)$$

$$\begin{aligned} N_{fi\{\mathbf{k}\}}^{\{\alpha,\eta\}\{s\}} &= \langle \bar{i} | \xi_{\alpha_1}^{-\eta_1, -\mathbf{k}_1} | \bar{s}_1 \rangle \dots \langle \bar{s}_{N-1} | \xi_{\alpha_N}^{-\eta_N, -\mathbf{k}_N} | \bar{f} \rangle \\ &= N_{\bar{i}\bar{f}\{r\}\{-\mathbf{k}\}}^{r\{\alpha, -\eta\}\{\rho(\bar{s})\}}, \end{aligned} \quad (3.6)$$

respectively. In these relations we have defined a permutation operation r that reverses the ordering of the labels $\{\alpha, \eta, \mathbf{k}\}$ appearing within a given contribution to the amplitude. For example, the ordering considered here is $1, \dots, N$ and under r this reverses to $N, \dots, 1$. We have also defined the palindromic reordering of the intermediate electronic states: $s_i \rightarrow \rho(s_i) = s_{N-i}$. The denominator factor (Eq.(2.18)) may be rewritten:

$$\begin{aligned} D_{fi}^{\{\eta\}\{s\}} &= \left((E_{f, s_{N-1}} + \hbar\eta_N\omega_N - i\Gamma_{s_{N-1}}) \dots \left(E_{f, s_1} + \hbar \sum_{p=2}^N \eta_p\omega_p - i\Gamma_{s_1} \right) \right)^* \\ &= \left(D_{if\{-\Gamma\}}^{r\{-\eta\}\{\rho(s)\}} \right)^*, \end{aligned} \quad (3.7)$$

$$\begin{aligned}
D_{fi}^{\{\eta\}\{s\}} &= \left((E_{i,s_1} - \hbar\eta_1\omega_1 - i\Gamma_{s_1}) \dots \left(E_{i,s_{N-1}} - \hbar \sum_{p=1}^{N-1} \eta_p\omega_p - i\Gamma_{s_{N-1}} \right) \right)^* \\
&= \left(D_{fi\{-\Gamma\}}^{\{\eta\}\{s\}} \right)^*, \tag{3.8}
\end{aligned}$$

$$\begin{aligned}
D_{fi}^{\{\eta\}\{s\}} &= (E_{f,s_{N-1}} + \hbar\eta_N\omega_N + i\Gamma_{s_{N-1}}) \dots \left(E_{f,s_1} + \hbar \sum_{p=2}^N \eta_p\omega_p + i\Gamma_{s_1} \right) \\
&= D_{if}^{r\{-\eta\}\{\rho(s)\}}, \tag{3.9}
\end{aligned}$$

where we have used the overall resonance condition $E_{i,f} = \sum_{p=1}^N \eta_p\omega_p$. In the first two relations the complex conjugation changes the sign of all the imaginary damping factors $i\Gamma$ within the energy denominators and is denoted by the $\{-\Gamma\}$ subscript.

Since the electronic Hamiltonian is time-even ($\mathcal{T}H_{\text{elec}}\mathcal{T}^{-1} = H_{\text{elec}}$), the unperturbed electronic energies satisfy [83]

$$E_s = E_{\bar{s}}. \tag{3.10}$$

Also, Andrews *et al.* [8] show that $\Gamma_s = \Gamma_{\bar{s}}$, so that the denominator factors are invariant under $\{s\} \rightarrow \{\bar{s}\}$. Hence, Eqs.(3.4) to (3.9) give

$$O_{fi\{\mathbf{k}\}}^{\{\alpha,\eta\}} \stackrel{\text{H}}{=} \sum_{\pi\{\alpha\},\{s\}} \left(\frac{N_{if\pi\{r\{\mathbf{k}\}\}}^{\pi\{r\{\alpha,-\eta\}\{\rho(s)\}}}}{D_{if\{-\Gamma\}}^{\pi\{r\{-\eta\}\{\rho(s)\}}}} \right)^* = \left(O_{if\{\mathbf{k}\}}^{\{\alpha,-\eta,-\Gamma\}} \right)^*, \tag{3.11}$$

$$O_{fi\{\mathbf{k}\}}^{\{\alpha,\eta\}} \stackrel{\text{T}}{=} \sum_{\pi\{\alpha\},\{s\}} \left(\frac{N_{fi\pi\{-\mathbf{k}\}}^{\pi\{\alpha,\eta\}\{\bar{s}\}}}{D_{fi\{-\Gamma\}}^{\pi\{\eta\}\{\bar{s}\}}} \right)^* = \left(O_{fi\{-\mathbf{k}\}}^{\{\alpha,\eta,-\Gamma\}} \right)^*, \tag{3.12}$$

$$O_{fi\{\mathbf{k}\}}^{\{\alpha,\eta\}} \stackrel{\text{HT}}{=} \sum_{\pi\{\alpha\},\{s\}} \frac{N_{if\pi\{r\{-\mathbf{k}\}\}}^{\pi\{r\{\alpha,-\eta\}\{\rho(\bar{s})\}}}}{D_{if}^{\pi\{r\{-\eta\}\{\rho(\bar{s})\}}}} = O_{if\{-\mathbf{k}\}}^{\{\alpha,-\eta\}}, \tag{3.13}$$

where the sum over permutations $\pi\{\alpha\}$ removes the need for the r . The change of sign of the $\{\eta\} \rightarrow \{-\eta\} = -\eta_1, \dots, -\eta_N$ in Eqs.(3.11) and (3.13) denotes that the input and output photons have been exchanged. The change of sign of the $\{\mathbf{k}\} \rightarrow \{-\mathbf{k}\}$ in Eqs.(3.12) and (3.13) denotes that the photon directions have been reversed. Because of the $\{\Gamma\} \rightarrow \{-\Gamma\}$ contained in the first two relations, the transformation of the amplitude under H and T results in an expression representing a new physical process only for the cases where damping may be neglected. When damping factors are included, only under HT does the transformation result in a new (time-reversed) process. The reasons for this are discussed in Chap. 6.

A derivation of these relations in the electric dipole approximation may be found in, for example, Butcher and Cotter [23], and the extension to higher multipoles in Stedman [129]; in these analyses damping factors are not included. Allowing

for intermediate resonances, Andrews *et al.* [8] have given H and HT symmetries on second-harmonic generation amplitudes in the electric dipole approximation. Equations (3.11) to (3.13) treat H, T and HT symmetries when both damping factors and all multipoles are included. Following the terminology of Stedman [129], these are the electronic parts of the reciprocity, conjugation and reversal theorems, the last of which relate the amplitudes of two time-reversed nonlinear optical processes, such as second-harmonic generation and parametric down-conversion.

Chapter 5 is based on Eq.(3.12) and the remaining chapters are based, directly or indirectly, on Eq.(3.13). Hermitian conjugation H is therefore an essential component within the derivation of most but not all of our ‘time reversal’ selection rules (this is also true for selection rules found in the literature). However, we shall loosely refer to both of the T and HT relations as following from ‘time reversal symmetry’, and only implicitly note the role of H. Incidentally, Eq.(3.11) bears a closer resemblance to the true time reversal symmetry relation of Eq.(3.13) than does Eq.(3.12).

Finally, we have not explicitly considered the quadratic terms, $\xi_{\alpha\alpha'}$ (Eq.(2.24)), in our derivations. As mentioned in §2.4.2, all derivations that hold true for terms involving only the linear interaction also hold for the terms in \mathcal{Q} which involve the quadratic interaction. We do not prove this in full detail here, as it would unnecessarily complicate our notation, but rather illustrate in §3.1.5 that it is true for the example of second-harmonic generation. For the general case we note the relations

$$\left(\xi_{\alpha\alpha'}^{\eta\eta',\mathbf{k}\mathbf{k}'}\right)^\dagger = \xi_{\alpha\alpha'}^{-\eta-\eta',\mathbf{k}\mathbf{k}'} \quad \left(\xi_{\alpha\alpha'}^{\eta\eta',\mathbf{k}\mathbf{k}'}\right) = \xi_{\alpha\alpha'}^{\eta\eta',-\mathbf{k}-\mathbf{k}'} \quad \left(\xi_{\alpha\alpha'}^{\eta\eta',\mathbf{k}\mathbf{k}'}\right)^\dagger = \xi_{\alpha\alpha'}^{-\eta-\eta',-\mathbf{k}-\mathbf{k}'} \quad (3.14)$$

which are exactly analogous to Eq.(3.3). It is therefore readily seen that a full verification would also be straightforward (if tedious). Note, the quadratic term associated with Rayleigh and Raman scattering simply involves the matrix element of $\xi_{\alpha\alpha'}^{\eta\eta',\mathbf{k}\mathbf{k}'}$ between the final and initial electronic states, so that Eq.(3.14) constitutes a verification for that example.

3.1.2 Photon field symmetries

We discuss phase conventions relating to the action of H, T and HT on the photon field.

The transverse electric field operator is of the form [94]:

$$\mathbf{E}(\mathbf{r}) = \sum_{\mathbf{k}} c_{\mathbf{k}} \left(i\phi_1 a_{\mathbf{k}} \mathbf{e}_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}} - i\phi_1^* a_{\mathbf{k}}^\dagger \mathbf{e}_{\mathbf{k}}^* e^{-i\mathbf{k}\cdot\mathbf{r}} \right), \quad (3.15)$$

where $\mathbf{e}_{\mathbf{k}} = \mathbf{e}_{\mathbf{k},j}$, j is 1, 2 for linear polarisations and $+, -$ for right and left circular polarisations. The phase ϕ_1 , which is not explicitly discussed by Loudon [94],

allows for example a relative phase of +1 between the annihilation and creation operators (see Stevens [132] for a discussion of this in the phonon context). Note, if matter is present the expression on the right hand side of Eq.(3.15) corresponds to the displacement operator \mathbf{D} rather than the electric field. However, because the displacement field operator is also time-even, the analysis of this section holds equally well in that case.

The time reversed electric field operator is

$$\bar{\mathbf{E}}(\mathbf{r}) = \sum_{\mathbf{k}} c_{\mathbf{k}} \left(-i\phi_1^* \phi_2 \phi_3 a_{\bar{\mathbf{k}}} \bar{\mathbf{e}}_{\bar{\mathbf{k}}} e^{-i\mathbf{k} \cdot \mathbf{r}} + i\phi_1 \phi_2^* \phi_3^* a_{\mathbf{k}}^{\dagger} \mathbf{e}_{\mathbf{k}} e^{i\mathbf{k} \cdot \mathbf{r}} \right), \quad (3.16)$$

where $\bar{\mathbf{k}} \equiv (-\mathbf{k}, j)$, and the phases ϕ_2, ϕ_3 are defined by

$$\bar{a}_{\mathbf{k}} = \phi_2 a_{\bar{\mathbf{k}}} \quad \bar{\mathbf{e}}_{\mathbf{k}} = \phi_3 \mathbf{e}_{\bar{\mathbf{k}}}. \quad (3.17)$$

These phases relate the otherwise strictly unconnected operators and polarisation vectors of the time reversed modes \mathbf{k} and $\bar{\mathbf{k}}$ [100]. Since \mathbf{E} is time-even, Eqs.(3.15) and (3.16) give the constraint

$$\phi_1^{*2} \phi_2 \phi_3 = -1 \quad (3.18)$$

(an identical constraint follows if the vector potential or magnetic field operators are considered). Hence, although these phases are highly underdetermined, the ‘natural’ choice of ignoring such phases is incorrect. Standard choices invariably begin in Eq.(3.15) with $\phi_1 = 1$, and then either have $\phi_2 = -1$ (e.g. Gottfried [48]) or $\phi_3 = -1$ (e.g. Loudon [93]). We believe the nonstandard choice of $\phi_1 = -i$, $\phi_2 = \phi_3 = 1$ is simplest, but we leave our phases as arbitrary; we return to this point later in this section. There exists further phase choices inasmuch as we could have subscripted our three phases with \mathbf{k} , however for notational convenience we have supposed the phases are independent of the mode label.

If the mode k_1 involves absorption then $\gamma_{\{\alpha\}}^{\{n'_k n_k\}}$ contains $i\phi_1 c_{k_1} \langle n_{k_1} - 1 | a_{k_1} | n_{k_1} \rangle (e_{k_1})_{\alpha_1}$ (Eq.(2.29)). Under H, T and HT the part $i\phi_1 (e_{k_1})_{\alpha_1}$ becomes

$$\left(-i\phi_1^* (e_{k_1}^*)_{\alpha_1} \right)^* \quad \phi_2 \left(i\phi_1 (e_{\bar{k}_1})_{\alpha_1} \right)^* \quad \phi_2 \left(-i\phi_1^* (e_{\bar{k}_1}^*)_{\alpha_1} \right) \quad (3.19)$$

respectively; if k_1 involves emission then ϕ_2^* replaces ϕ_2 . This ϕ_2 dependence is obtained indirectly through $\bar{\mathbf{e}}_{\mathbf{k}} = \phi_3 \mathbf{e}_{\bar{\mathbf{k}}}$ together with Eq.(3.18). The real number $c_{\mathbf{k}}$ satisfies $c_{\mathbf{k}} = c_{\bar{\mathbf{k}}}$. Because $|\bar{n}_{\mathbf{k}}\rangle = \phi_2^{-n_{\mathbf{k}}} |n_{\bar{\mathbf{k}}}\rangle$, no ϕ_2 dependence arises from the photon matrix elements under these symmetries, e.g.

$$\langle n_{\mathbf{k}} - 1 | a_{\mathbf{k}} | n_{\mathbf{k}} \rangle = \langle n_{\bar{\mathbf{k}}} | a_{\bar{\mathbf{k}}}^{\dagger} | n_{\bar{\mathbf{k}}} - 1 \rangle. \quad (3.20)$$

Thus the photon parts of the amplitude satisfy,

$$\gamma_{\{\alpha\}}^{\{n'_k n_k\}} \stackrel{\text{H}}{=} \gamma_{\{\alpha\}}^{\{n_k n'_k\}} \quad \gamma_{\{\alpha\}}^{\{n'_k n_k\}} \stackrel{\text{T}}{=} \phi_2^Z \gamma_{\{\alpha\}}^{\{n'_k n_k\}} \quad \gamma_{\{\alpha\}}^{\{n'_k n_k\}} \stackrel{\text{HT}}{=} \phi_2^Z \gamma_{\{\alpha\}}^{\{n_k n'_k\}} \quad (3.21)$$

where $Z = Z_- - Z_+$, Z_- being the number of photons absorbed and Z_+ the number emitted ($Z_- + Z_+ = N$).

As mentioned, we advocate $\phi_1 = -i$, whereas standard treatments of quantised electromagnetic fields have $\phi_1 = +1$. It is therefore worth checking that our preferred phase choice is valid. To do this we follow the discussion of Cohen-Tannoudji *et al.* [33] on quantising the radiation field, but with an arbitrary ϕ_1 included. Consider the normal coordinate, ϑ_j , of the classical electromagnetic field that is defined by (in Ref. [33] $\phi_1 = +1$)

$$\vartheta_j(\mathbf{k}, t) = \frac{-i}{2} \phi_1 \sqrt{\frac{2\varepsilon_0}{\hbar\omega_k}} \left(\mathcal{E}_j(\mathbf{k}, t) - \left(c\hat{\mathbf{k}} \times \mathcal{B}(\mathbf{k}, t) \right)_j \right), \quad (3.22)$$

where $\mathcal{E}_j(\mathbf{k}, t)$ and $\mathcal{B}_j(\mathbf{k}, t)$ are Fourier components of the classical transverse electric and magnetic fields; $j = 1, 2$. Following the analysis in Ref. [33] this normal coordinate may be re-expressed as

$$\vartheta_j(\mathbf{k}, t) = \phi_1 \sqrt{\frac{\varepsilon_0}{2\hbar\omega_k}} (\omega \mathcal{A}_j(\mathbf{k}, t) - i\mathcal{E}_j(\mathbf{k}, t)), \quad (3.23)$$

where $\mathcal{A}_j(\mathbf{k}, t)$ is a Fourier component of the classical transverse vector potential. Once again an identical expression exists Ref. [33] but with $\phi_1 = +1$. For a free radiation field $\mathcal{A}_j(\mathbf{k}, t)$ and $\mathcal{E}_j(\mathbf{k}, t)$ form a pair of canonical coordinates, and therefore under the canonical quantisation procedure

$$\vartheta_j(\mathbf{k}) \rightarrow a_k \quad \vartheta_j^*(\mathbf{k}) \rightarrow a_k^\dagger. \quad (3.24)$$

This, along with other standard results, follows regardless of the value of ϕ_1 . We have thus verified that we are free to set the phase ϕ_1 in Eq.(3.15) to whichever value is most convenient; the value $\phi_1 = -i$ gives a simplified form for $\mathbf{E}(\mathbf{r})$ and $\mathbf{B}(\mathbf{r})$.

3.1.3 Full symmetries: Reversality theorems

We combine the results of the previous two sections to give the H, T and HT symmetries on the full transition amplitude $V_{fi}^{\{n'_k n_k\}}$. Equations (3.11) to (3.13) and (3.21) together give

$$V_{fi}^{\{n'_k n_k\}} \stackrel{\text{H}}{=} \left(V_{if}^{\{n_k n'_k, -\Gamma\}} \right)^*, \quad (3.25)$$

$$V_{fi}^{\{n'_k n_k\}} \stackrel{\text{T}}{=} \phi_2^Z \left(V_{\bar{f}\bar{i}}^{\{n'_k n_k, -\Gamma\}} \right)^*, \quad (3.26)$$

$$V_{fi}^{\{n'_k n_k\}} \stackrel{\text{HT}}{=} \phi_2^Z V_{\bar{i}\bar{f}}^{\{n_k n'_k\}}, \quad (3.27)$$

the $-\Gamma$ has the same meaning as in Eqs.(3.11) and (3.12). The reciprocity theorem, based on H alone, relates amplitudes for situations in which in and out states are exchanged (Fig. 3.1). The conjugation theorem is based on T alone

and relates amplitudes for situations in which each electronic and photon state is time-reversed (Fig. 3.2). As discussed for Eqs.(3.11) and (3.12), such interpretations are only valid when damping factors may be ignored. This relates to the discussion of Berger [17], who argues there is no reason why reciprocity (Berger's "microscopic invertibility") should in general be a valid symmetry; see also Chap. 6. The final relation is the reversal theorem, where in and out states are exchanged and each electronic and photon state is time-reversed (Fig. 3.3). It is the reversal theorem which corresponds to time reversal symmetry in nonlinear optics. Equation (3.13) may be considered to be a special case of the general discussion given in §2.1 on the equivalence between time reversal symmetry and motion reversal symmetry. In particular, Eq.(3.13) states that the amplitude for the process $|i\rangle|\{n_k\}\rangle \rightarrow |f\rangle|\{n'_k\}\rangle$ is the same as the amplitude for the motion reversed scenario: $|\bar{f}\rangle|\{n_{\bar{k}}'\}\rangle \rightarrow |\bar{i}\rangle|\{n_{\bar{k}}\}\rangle$ (see Fig. 2.2).

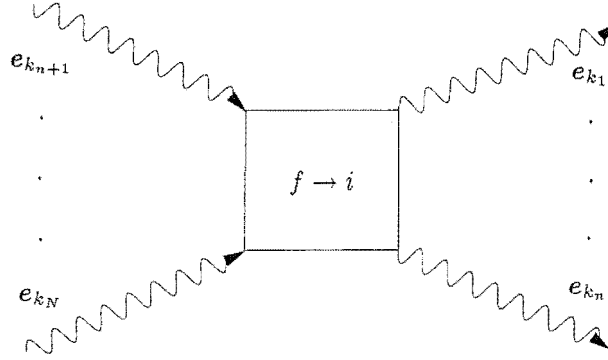


Fig. 3.1: In the absence of damping factors H symmetry relates processes where the in and out states are interchanged (compare with Fig. 2.3).

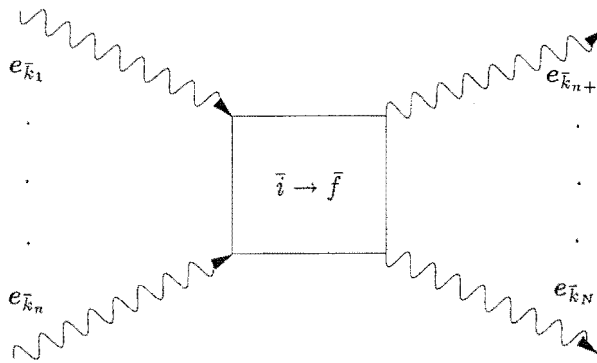


Fig. 3.2: In the absence of damping factors T symmetry relates processes where the light-matter states are time-reversed (compare with Fig. 2.3).

The distinction between reciprocity, conjugation and reversal help in resolving the differing approaches of Svirkov and Zheludev [133] and of Andrews [7] in a discussion of what constitutes time reversal. To Andrews [7], time reversal implies that all photon wavevectors reverse, $\{\mathbf{k}\} \rightarrow \{-\mathbf{k}\}$, and that input and

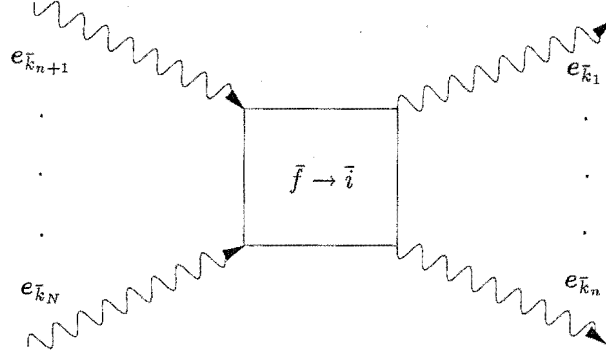


Fig. 3.3: HT symmetry relates two time-reversed processes, i.e. where the in and out states are interchanged and time-reversed (compare with Fig. 2.3).

output states (of matter and radiation) are interchanged. The symmetry relevant to Andrews' discussion is thus the reversal theorem. Figure 3 of Svirkov and Zheludev [133], under discussion by Andrews and supposedly describing a direct and a time-reversed scenario, corresponds to none of these three symmetries, in that only initial momenta are reversed (this figure also appears in Zheludev *et al.* [143] as their figure 1).

3.1.4 Examples

We give two examples to illustrate these symmetries; as in §2.4.3 these are Rayleigh scattering and second-harmonic generation. Consider first Rayleigh scattering. H symmetry gives

$$\text{Eq. (2.31)} \stackrel{\text{H}}{=} \left\{ c_{k_1} c_{k_2} \langle n_{k_1} | a_{k_1}^\dagger | n_{k_1} - 1 \rangle \langle n_{k_2} | a_{k_2} | n_{k_2} + 1 \rangle (e_{k_1}^*)_{\alpha_1} (e_{k_2})_{\alpha_2} \right\}^*; \quad (3.28)$$

$$\begin{aligned} \text{Eq. (2.32)} &\stackrel{\text{H}}{=} \sum_{s_1} \frac{\langle i | \xi_{\alpha_1}^{+, k_1} | s_1 \rangle^* \langle s_1 | \xi_{\alpha_2}^{-, k_2} | f \rangle^*}{E_{i, s_1} + \hbar\omega_1 + i\Gamma_{s_1}} + \frac{\langle i | \xi_{\alpha_2}^{-, k_2} | s_1 \rangle^* \langle s_1 | \xi_{\alpha_1}^{+, k_1} | i \rangle^*}{E_{i, s_1} - \hbar\omega_1 + i\Gamma_{s_1}} \\ &= \left\{ \sum_{s_1} \frac{\langle i | \xi_{\alpha_1}^{+, k_1} | s_1 \rangle \langle s_1 | \xi_{\alpha_2}^{-, k_2} | f \rangle}{E_{f, s_1} + \hbar\omega_1 - i\Gamma_{s_1}} + \frac{\langle i | \xi_{\alpha_2}^{-, k_2} | s_1 \rangle \langle s_1 | \xi_{\alpha_1}^{+, k_1} | f \rangle}{E_{f, s_1} - \hbar\omega_1 - i\Gamma_{s_1}} \right\}^* \end{aligned} \quad (3.29)$$

where the first step involves applying H to the matrix elements (Eq.(3.4)) and the second rewriting the denominator (Eq.(3.7)). Together these two relations illustrate Eq.(3.25) for Rayleigh scattering (Fig. 3.4).

T symmetry gives

$$\text{Eq. (2.31)} \stackrel{\text{T}}{=} \left\{ c_{\vec{k}_1} c_{\vec{k}_2} \langle n_{\vec{k}_1} - 1 | a_{\vec{k}_1} | n_{\vec{k}_1} \rangle \langle n_{\vec{k}_2} + 1 | a_{\vec{k}_2}^\dagger | n_{\vec{k}_2} \rangle (e_{\vec{k}_1})_{\alpha_1} (e_{\vec{k}_2}^*)_{\alpha_2} \right\}^*; \quad (3.30)$$

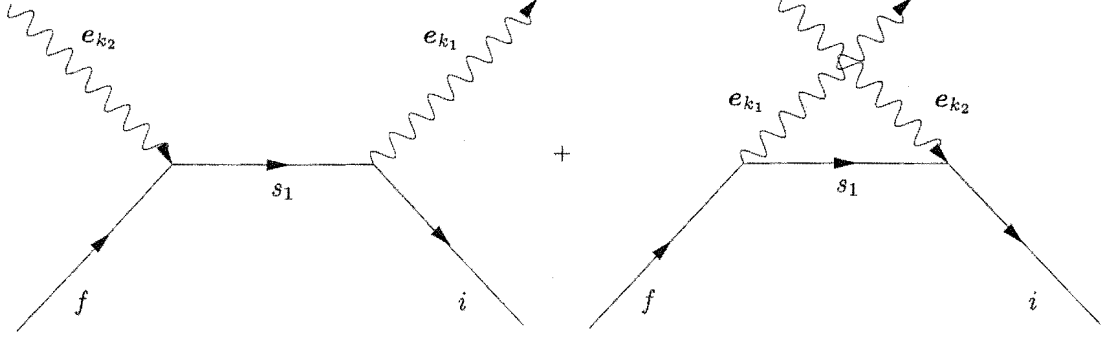


Fig. 3.4: H symmetry as applied to Rayleigh scattering when damping factors may be neglected (compare with Fig. 2.4). The input photon of the original process (1) is now created and the original output photon (2) is now absorbed. Similarly, the initial and final electronic states are interchanged.

$$\text{Eq. (2.32)} \stackrel{\text{T}}{=} \left\{ \sum_{s_1} \frac{\langle \bar{f} | \xi_{\alpha_2}^{+, -k_2} | s_1 \rangle \langle s_1 | \xi_{\alpha_1}^{-, -k_1} | \bar{i} \rangle}{E_{\bar{i}, s_1} + \hbar\omega_1 - i\Gamma_{s_1}} + \frac{\langle \bar{f} | \xi_{\alpha_1}^{-, -k_1} | s_1 \rangle \langle s_1 | \xi_{\alpha_2}^{+, -k_2} | \bar{i} \rangle}{E_{\bar{i}, s_1} - \hbar\omega_1 - i\Gamma_{s_1}} \right\}^*, \quad (3.31)$$

where Eq.(3.31) involves applying T to the matrix elements (Eq.(3.5)), rewriting the denominator (Eq.(3.8)) and $\{s\} \rightarrow \{\bar{s}\}$ (Eq.(3.10)); Eq.(3.30) follows from Eq.(3.21). Together these two relations illustrate Eq.(3.26) for Rayleigh scattering (Fig. 3.5).

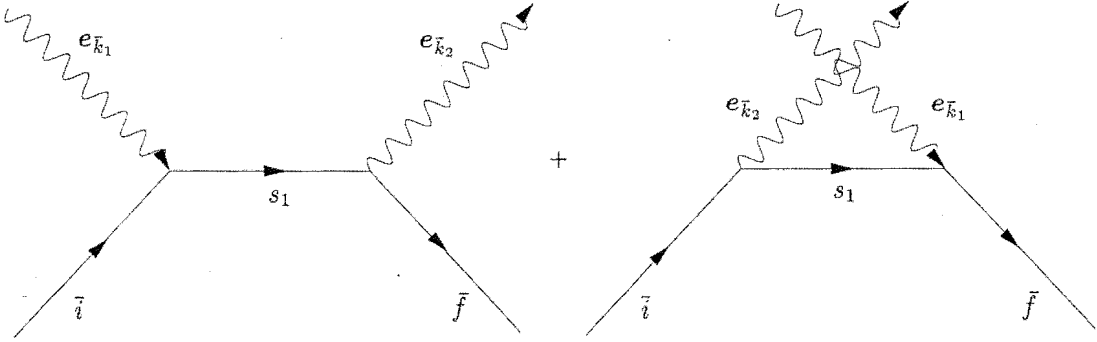


Fig. 3.5: T symmetry as applied to Rayleigh scattering when damping factors may be neglected (compare with Fig. 2.4). The photons modes are time-reversed (i.e. have reversed wavevectors) and the electronic states are also replaced by their T-conjugates.

Similarly, HT symmetry gives

$$\text{Eq. (2.31)} \stackrel{\text{HT}}{=} c_{\bar{k}_1} c_{\bar{k}_2} \langle n_{\bar{k}_1} | a_{\bar{k}_1}^\dagger | n_{\bar{k}_1} - 1 \rangle \langle n_{\bar{k}_2} | a_{\bar{k}_2} | n_{\bar{k}_2} + 1 \rangle (e_{\bar{k}_1}^*)_{\alpha_1} (e_{\bar{k}_2})_{\alpha_2}, \quad (3.32)$$

$$\text{Eq. (2.32)} \stackrel{\text{HT}}{=} \sum_{s_1} \frac{\langle \bar{i} | \xi_{\alpha_1}^{+, -k_1} | s_1 \rangle \langle s_1 | \xi_{\alpha_2}^{-, -k_2} | \bar{f} \rangle}{E_{\bar{f}, s_1} + \hbar\omega_1 + i\Gamma_{s_1}} + \frac{\langle \bar{i} | \xi_{\alpha_2}^{-, -k_2} | s_1 \rangle \langle s_1 | \xi_{\alpha_1}^{+, -k_1} | \bar{f} \rangle}{E_{\bar{f}, s_1} - \hbar\omega_1 + i\Gamma_{s_1}}, \quad (3.33)$$

illustrating Eq.(3.27) (Fig. 3.6).

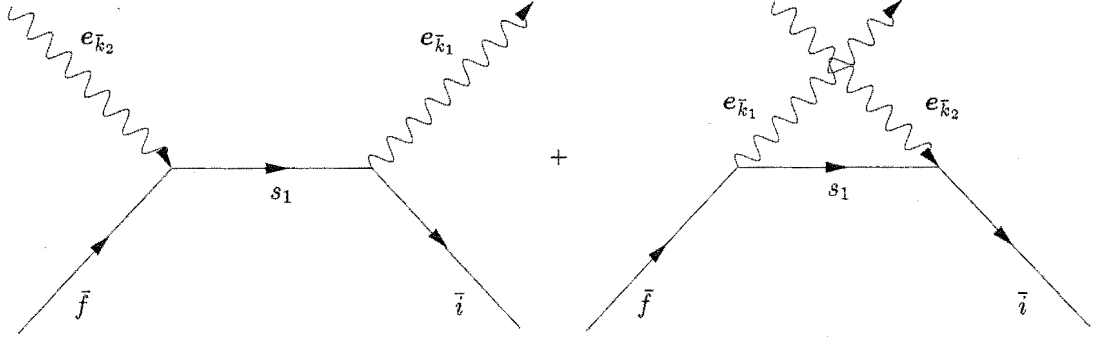


Fig. 3.6: HT symmetry as applied to Rayleigh scattering (compare with Fig. 2.4). The input and output photons are interchanged and have reversed wavevectors. Similarly, the initial and final electronic states are interchanged and time-reversed.

Consider next the behaviour of the second-harmonic generation amplitude under these three symmetries (see also Figs. 3.7 to 3.9): Eq.(2.38) $\stackrel{H}{=} \{-i\phi_1^* c_{k_1}^2 c_{k_3} \times$

$$\langle n_{k_1} - 1 | a_{k_1}^\dagger | n_{k_1} - 2 \rangle \langle n_{k_1} | a_{k_1}^\dagger | n_{k_1} - 1 \rangle \langle n_{k_3} | a_{k_3} | n_{k_3} + 1 \rangle (e_{k_1}^*)_{\alpha_1} (e_{k_1}^*)_{\alpha_2} (e_{k_3})_{\alpha_3} \}^*, \quad (3.34)$$

$$\begin{aligned} \text{Eq.(2.39)} \stackrel{H}{=} & \left\{ \sum_{s_1, s_2} \frac{\langle i | \xi_{\alpha_1}^{+, k_1} | s_2 \rangle \langle s_2 | \xi_{\alpha_2}^{+, k_1} | s_1 \rangle \langle s_1 | \xi_{\alpha_3}^{-, k_3} | f \rangle}{(E_{f, s_1} + \hbar\omega_3 - i\Gamma_{s_1}) (E_{f, s_2} + \hbar\omega_3 - \hbar\omega_1 - i\Gamma_{s_2})} \right. \\ & + \frac{\langle i | \xi_{\alpha_1}^{+, k_1} | s_2 \rangle \langle s_2 | \xi_{\alpha_3}^{-, k_3} | s_1 \rangle \langle s_1 | \xi_{\alpha_2}^{+, k_1} | f \rangle}{(E_{f, s_1} - \hbar\omega_1 - i\Gamma_{s_1}) (E_{f, s_2} - \hbar\omega_1 + \hbar\omega_3 - i\Gamma_{s_2})} \\ & \left. + \frac{\langle i | \xi_{\alpha_3}^{-, k_3} | s_2 \rangle \langle s_2 | \xi_{\alpha_2}^{+, k_1} | s_1 \rangle \langle s_1 | \xi_{\alpha_1}^{+, k_1} | f \rangle}{(E_{f, s_1} - \hbar\omega_1 - i\Gamma_{s_1}) (E_{f, s_2} - 2\hbar\omega_1 - i\Gamma_{s_2})} \right\}^*; \quad (3.35) \end{aligned}$$

$$\text{Eq.(2.38)} \stackrel{T}{=} \phi_2 \{ i\phi_1 c_{k_1}^2 c_{k_3} \times$$

$$\langle n_{\bar{k}_1} - 2 | a_{\bar{k}_1} | n_{\bar{k}_1} - 1 \rangle \langle n_{\bar{k}_1} - 1 | a_{\bar{k}_1} | n_{\bar{k}_1} \rangle \langle n_{\bar{k}_3} + 1 | a_{\bar{k}_3}^\dagger | n_{\bar{k}_3} \rangle (e_{\bar{k}_1})_{\alpha_1} (e_{\bar{k}_1})_{\alpha_2} (e_{\bar{k}_3}^*)_{\alpha_3} \}^*, \quad (3.36)$$

$$\begin{aligned} \text{Eq.(2.39)} \stackrel{T}{=} & \left\{ \sum_{s_1, s_2} \frac{\langle \bar{f} | \xi_{\alpha_3}^{+, -k_3} | s_2 \rangle \langle s_2 | \xi_{\alpha_2}^{-, -k_1} | s_1 \rangle \langle s_1 | \xi_{\alpha_1}^{-, -k_1} | \bar{i} \rangle}{(E_{\bar{i}, s_1} + \hbar\omega_1 - i\Gamma_{s_1}) (E_{\bar{i}, s_2} + 2\hbar\omega_1 - i\Gamma_{s_2})} \right. \\ & + \frac{\langle \bar{f} | \xi_{\alpha_2}^{-, -k_1} | s_2 \rangle \langle s_2 | \xi_{\alpha_3}^{+, -k_3} | s_1 \rangle \langle s_1 | \xi_{\alpha_1}^{-, -k_1} | \bar{i} \rangle}{(E_{\bar{i}, s_1} + \hbar\omega_1 - i\Gamma_{s_1}) (E_{\bar{i}, s_2} + \hbar\omega_1 - \hbar\omega_3 - i\Gamma_{s_2})} \\ & \left. + \frac{\langle \bar{f} | \xi_{\alpha_1}^{-, -k_1} | s_2 \rangle \langle s_2 | \xi_{\alpha_2}^{-, -k_1} | s_1 \rangle \langle s_1 | \xi_{\alpha_3}^{+, -k_3} | \bar{i} \rangle}{(E_{\bar{i}, s_1} - \hbar\omega_3 - i\Gamma_{s_1}) (E_{\bar{i}, s_2} - \hbar\omega_3 + \hbar\omega_1 - i\Gamma_{s_2})} \right\}^*; \quad (3.37) \end{aligned}$$

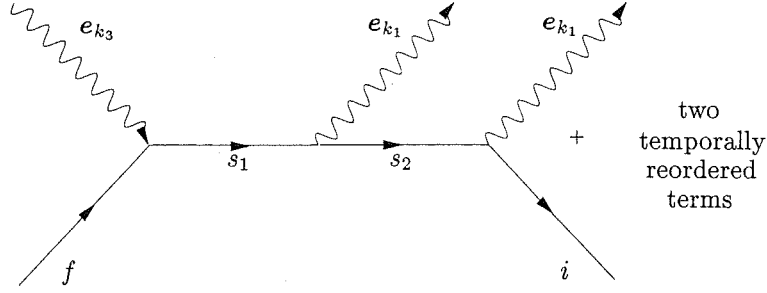


Fig. 3.7: H symmetry as applied to second-harmonic generation when damping factors may be neglected (compare with Fig. 2.5). The interchange of input and output states converts the process into parametric down-conversion. The temporal ordering shown is for photon 3 absorbed and 1 and 2 emitted, this corresponds to the first term in Eq.(3.35) (i.e. H symmetry applied to the diagram shown in Fig. 2.5).

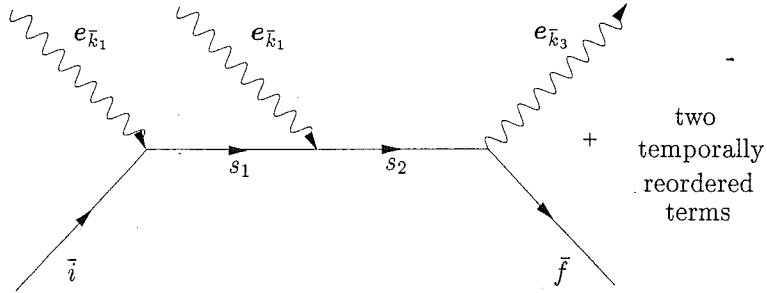


Fig. 3.8: T symmetry as applied to second-harmonic generation when damping factors may be neglected (compare with Fig. 2.5). As in Rayleigh scattering (Fig. 3.5) the states are all time-reversed.

$$\text{Eq.}(2.38) \stackrel{\text{HT}}{=} \phi_2 \{ -i\phi_1^* c_{\bar{k}_1}^2 c_{\bar{k}_3} \times$$

$$\langle n_{\bar{k}_1} - 1 | a_{\bar{k}_1}^\dagger | n_{\bar{k}_1} - 2 \rangle \langle n_{\bar{k}_1} | a_{\bar{k}_1}^\dagger | n_{\bar{k}_1} - 1 \rangle \langle n_{\bar{k}_3} | a_{\bar{k}_3} | n_{\bar{k}_3} + 1 \rangle (e_{\bar{k}_1}^*)_{\alpha_1} (e_{\bar{k}_1}^*)_{\alpha_2} (e_{\bar{k}_3})_{\alpha_3} \}, \quad (3.38)$$

$$\begin{aligned} \text{Eq.}(2.39) \stackrel{\text{HT}}{=} & \sum_{s_1, s_2} \frac{\langle \bar{i} | \xi_{\alpha_1}^{+, -\mathbf{k}_1} | s_2 \rangle \langle s_2 | \xi_{\alpha_2}^{+, -\mathbf{k}_1} | s_1 \rangle \langle s_1 | \xi_{\alpha_3}^{-, -\mathbf{k}_3} | \bar{f} \rangle}{(E_{\bar{f}, s_1} + \hbar\omega_3 + i\Gamma_{s_1}) (E_{\bar{f}, s_2} + \hbar\omega_3 - \hbar\omega_1 + i\Gamma_{s_2})} \\ & + \frac{\langle \bar{i} | \xi_{\alpha_1}^{+, -\mathbf{k}_1} | s_2 \rangle \langle s_2 | \xi_{\alpha_3}^{-, -\mathbf{k}_3} | s_1 \rangle \langle s_1 | \xi_{\alpha_2}^{+, -\mathbf{k}_1} | \bar{f} \rangle}{(E_{\bar{f}, s_1} - \hbar\omega_1 + i\Gamma_{s_1}) (E_{\bar{f}, s_2} - \hbar\omega_1 + \hbar\omega_3 + i\Gamma_{s_2})} \\ & + \frac{\langle \bar{i} | \xi_{\alpha_3}^{-, -\mathbf{k}_3} | s_2 \rangle \langle s_2 | \xi_{\alpha_2}^{+, -\mathbf{k}_1} | s_1 \rangle \langle s_1 | \xi_{\alpha_1}^{+, -\mathbf{k}_1} | \bar{f} \rangle}{(E_{\bar{f}, s_1} - \hbar\omega_1 + i\Gamma_{s_1}) (E_{\bar{f}, s_2} - 2\hbar\omega_1 + i\Gamma_{s_2})}. \end{aligned} \quad (3.39)$$

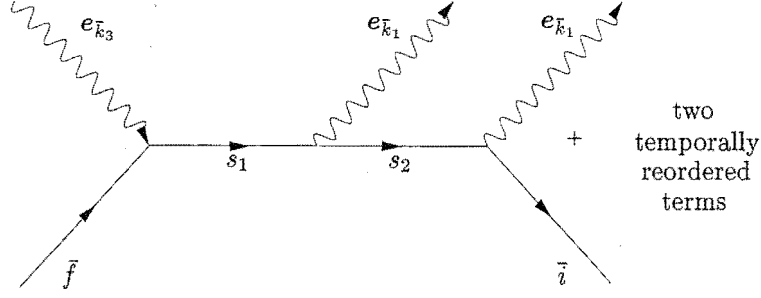


Fig. 3.9: HT symmetry as applied to second-harmonic generation (compare with Fig. 2.5). As in Fig. 3.7 the transformed process is parametric down-conversion, representing the time reverse of the original process. The temporal ordering shown corresponds to the first term in Eq.(3.39) (i.e. HT symmetry applied to the diagram shown in Fig. 2.5).

3.1.5 Aside: Quadratic terms for second-harmonic generation

The quadratic terms, $\mathcal{Q}|_{\text{SHG}}$, that are associated with the second-harmonic generation amplitude are (Fig. 3.10):

$$\begin{aligned} \mathcal{Q}|_{\text{SHG}} = & \sum_{s_1} \frac{\langle f | \xi_{\alpha_3}^{+, k_3} | s_1 \rangle \langle s_1 | \xi_{\alpha_1 \alpha_2}^{--, k_1 k_2} | i \rangle}{E_{i, s_1} + 2\hbar\omega_1 + i\Gamma_{s_1}} + \frac{\langle f | \xi_{\alpha_1 \alpha_2}^{--, k_1 k_2} | s_1 \rangle \langle s_1 | \xi_{\alpha_3}^{+, k_3} | i \rangle}{E_{i, s_1} - \hbar\omega_3 + i\Gamma_{s_1}} \\ & + \frac{\langle f | \xi_{\alpha_1}^{-, k_1} | s_1 \rangle \langle s_1 | \xi_{\alpha_2 \alpha_3}^{--, k_1 k_3} | i \rangle}{E_{i, s_1} + \hbar\omega_1 - \hbar\omega_3 + i\Gamma_{s_1}} + \frac{\langle f | \xi_{\alpha_2 \alpha_3}^{--, k_1 k_3} | s_1 \rangle \langle s_1 | \xi_{\alpha_1}^{-, k_1} | i \rangle}{E_{i, s_1} + \hbar\omega_1 + i\Gamma_{s_1}}. \end{aligned} \quad (3.40)$$

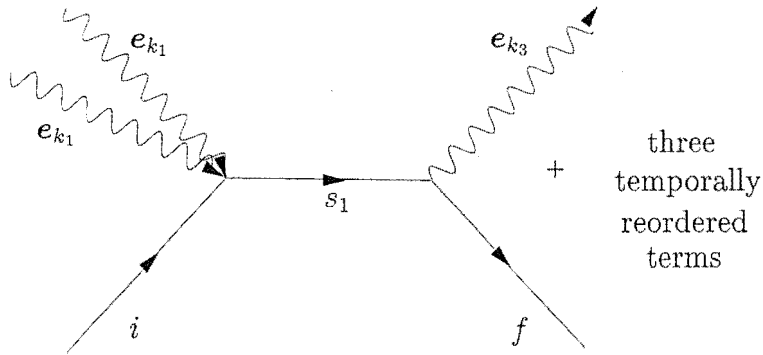


Fig. 3.10: The diagrammatic representation of the lowest order contributions to second-harmonic generation which involve the quadratic interaction. The ordering shown is for 1 and 2 absorbed, 3 emitted, given by the first term in Eq.(3.40).

We follow the methods of §3.1.1 to verify that the application of H, T and HT to this expression gives precisely the same results as were found in §3.1.4 for the terms involving only the linear interaction, $\xi_{\alpha}^{\eta, k}$ (see also Figs. 3.11 to 3.13).

$$Q|_{\text{SHG}} \stackrel{\text{H}}{=} \left\{ \sum_{s_1} \frac{\langle i|\xi_{\alpha_1\alpha_2}^{++,\mathbf{k}_1\mathbf{k}_2}|s_1\rangle\langle s_1|\xi_{\alpha_3}^{-,\mathbf{k}_3}|f\rangle}{E_{f,s_1} + \hbar\omega_3 - i\Gamma_{s_1}} + \frac{\langle i|\xi_{\alpha_3}^{-,\mathbf{k}_3}|s_1\rangle\langle s_1|\xi_{\alpha_1\alpha_2}^{++,\mathbf{k}_1\mathbf{k}_2}|f\rangle}{E_{f,s_1} - 2\hbar\omega_1 - i\Gamma_{s_1}} \right. \\ \left. + \frac{\langle i|\xi_{\alpha_2\alpha_3}^{+-,\mathbf{k}_1\mathbf{k}_3}|s_1\rangle\langle s_1|\xi_{\alpha_1}^{+,\mathbf{k}_1}|f\rangle}{E_{f,s_1} - \hbar\omega_1 - i\Gamma_{s_1}} + \frac{\langle i|\xi_{\alpha_1}^{+,\mathbf{k}_1}|s_1\rangle\langle s_1|\xi_{\alpha_2\alpha_3}^{+-,\mathbf{k}_1\mathbf{k}_3}|f\rangle}{E_{f,s_1} - \hbar\omega_1 + \hbar\omega_3 - i\Gamma_{s_1}} \right\}^* \quad (3.41)$$

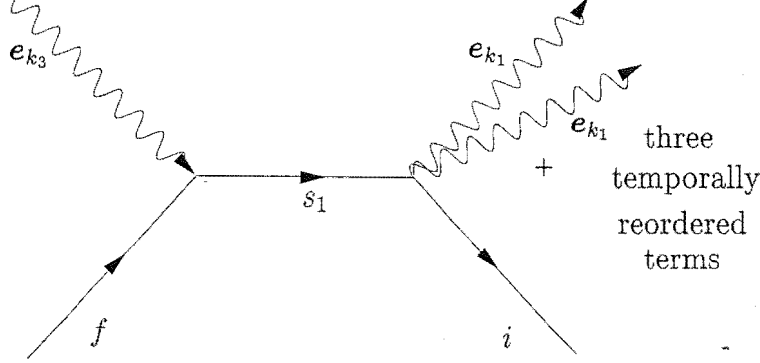


Fig. 3.11: H symmetry as applied to the quadratic terms in the second-harmonic generation amplitude when damping factors may be neglected (compare with Fig. 3.10). The resulting expressions correspond to the quadratic terms for parametric down-conversion. The temporal ordering shown is for photon 3 absorbed and 1 and 2 emitted, this corresponds to the first term in Eq.(3.41) (i.e. H symmetry applied to the diagram shown in Fig. 3.10).

$$Q|_{\text{SHG}} \stackrel{\text{T}}{=} \left\{ \sum_{s_1} \frac{\langle \bar{f}|\xi_{\alpha_3}^{+,-\mathbf{k}_3}|s_1\rangle\langle s_1|\xi_{\alpha_1\alpha_2}^{-,-\mathbf{k}_1-\mathbf{k}_2}|\bar{i}\rangle}{E_{\bar{i},s_1} + 2\hbar\omega_1 - i\Gamma_{s_1}} + \frac{\langle \bar{f}|\xi_{\alpha_1\alpha_2}^{-,-\mathbf{k}_1-\mathbf{k}_2}|s_1\rangle\langle s_1|\xi_{\alpha_3}^{+,-\mathbf{k}_3}|\bar{i}\rangle}{E_{\bar{i},s_1} - \hbar\omega_3 - i\Gamma_{s_1}} \right. \\ \left. + \frac{\langle \bar{f}|\xi_{\alpha_1}^{-,-\mathbf{k}_1}|s_1\rangle\langle s_1|\xi_{\alpha_2\alpha_3}^{-,-\mathbf{k}_1-\mathbf{k}_3}|\bar{i}\rangle}{E_{\bar{i},s_1} + \hbar\omega_1 - \hbar\omega_3 - i\Gamma_{s_1}} + \frac{\langle \bar{f}|\xi_{\alpha_2\alpha_3}^{-,-\mathbf{k}_1-\mathbf{k}_3}|s_1\rangle\langle s_1|\xi_{\alpha_1}^{-,-\mathbf{k}_1}|\bar{i}\rangle}{E_{\bar{i},s_1} + \hbar\omega_1 - i\Gamma_{s_1}} \right\}^* \quad (3.42)$$

$$Q|_{\text{SHG}} \stackrel{\text{HT}}{=} \sum_{s_1} \frac{\langle \bar{i}|\xi_{\alpha_1\alpha_2}^{++,-\mathbf{k}_1-\mathbf{k}_2}|s_1\rangle\langle s_1|\xi_{\alpha_3}^{-,-\mathbf{k}_3}|\bar{f}\rangle}{E_{\bar{f},s_1} + \hbar\omega_3 + i\Gamma_{s_1}} + \frac{\langle \bar{i}|\xi_{\alpha_3}^{-,-\mathbf{k}_3}|s_1\rangle\langle s_1|\xi_{\alpha_1\alpha_2}^{++,-\mathbf{k}_1-\mathbf{k}_2}|\bar{f}\rangle}{E_{\bar{f},s_1} - 2\hbar\omega_1 + i\Gamma_{s_1}} \\ + \frac{\langle \bar{i}|\xi_{\alpha_2\alpha_3}^{+-,-\mathbf{k}_1-\mathbf{k}_3}|s_1\rangle\langle s_1|\xi_{\alpha_1}^{+,-\mathbf{k}_1}|\bar{f}\rangle}{E_{\bar{f},s_1} - \hbar\omega_1 + i\Gamma_{s_1}} + \frac{\langle \bar{i}|\xi_{\alpha_1}^{+,-\mathbf{k}_1}|s_1\rangle\langle s_1|\xi_{\alpha_2\alpha_3}^{+-,-\mathbf{k}_1-\mathbf{k}_3}|\bar{f}\rangle}{E_{\bar{f},s_1} - \hbar\omega_1 + \hbar\omega_3 + i\Gamma_{s_1}} \quad (3.43)$$

3.1.6 Reversality theorems in the Coulomb gauge

We verify that identical reversality theorems are found in the Coulomb gauge. As discussed in §2.5, if the damping factors Γ are included, the Coulomb gauge

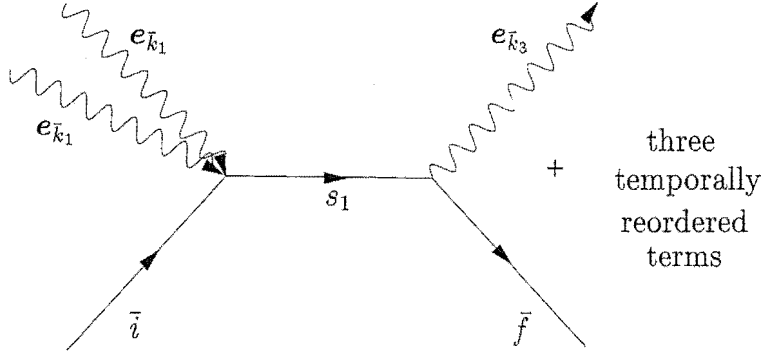


Fig. 3.12: T symmetry as applied to the quadratic terms for second-harmonic generation when damping factors may be neglected (compare with Fig. 3.10). The ordering shown is for 1 and 2 absorbed, 3 emitted, given by the first term in Eq.(3.42) (i.e. T symmetry applied to the diagram shown in Fig. 3.10).

amplitude cannot be obtained by a replacement of interaction Hamiltonians ($\xi \rightarrow \xi_{\text{Coul}}$). We therefore only consider the case where the damping factors may be neglected. (Note however, because those factors have been included in such a manner as to preserve HT symmetry (Chap. 6), identical theorems occur in the Coulomb gauge even if they are included.)

The Coulomb gauge interaction Hamiltonian possesses the symmetries

$$\left(\xi_{\alpha;\text{Coul}}^{\eta,\mathbf{k}}\right)^\dagger = \xi_{\alpha;\text{Coul}}^{-\eta,\mathbf{k}} \quad \left(\overline{\xi_{\alpha;\text{Coul}}^{\eta,\mathbf{k}}}\right) = -\xi_{\alpha;\text{Coul}}^{\eta,-\mathbf{k}} \quad \left(\overline{\xi_{\alpha;\text{Coul}}^{\eta,\mathbf{k}}}\right)^\dagger = -\xi_{\alpha;\text{Coul}}^{-\eta,-\mathbf{k}}, \quad (3.44)$$

the quadratic parts possess the same symmetry relations as in multipolar gauge (Eq.(3.14)). The time reversal phase of -1 occurs because the momentum operator is time-odd: $\mathbf{T}\mathbf{p}\mathbf{T}^{-1} = -\mathbf{p}$; such a phase does not occur due to the ‘magnetic’ interactions in the multipolar gauge (the terms on the second line of Eq.(2.22)) because the -1 is absorbed into the $\hat{\mathbf{k}} \rightarrow -\hat{\mathbf{k}}$. Following the analysis in §3.1.1, the electronic parts of the transition amplitude transform under H, T and HT to

$$\left(O_{i\bar{f}\{\mathbf{k}\};\text{Coul}}^{\{\alpha,-\eta\}}\right)^* \quad (-1)^N \left(O_{\bar{f}\bar{i}\{-\mathbf{k}\};\text{Coul}}^{\{\alpha,\eta\}}\right)^* \quad (-1)^N O_{\bar{i}\bar{f}\{-\mathbf{k}\};\text{Coul}}^{\{\alpha,-\eta\}}, \quad (3.45)$$

remembering that we have set $\Gamma = 0$. In considering the photon parts we note that if the mode k_1 involves absorption then $\gamma_{\{\alpha\}}^{\{n_k, n_k\}}$ contains $\phi_1 \omega_{k_1}^{-1} c_{k_1} \langle n_{k_1} - 1 | a_{k_1} | n_{k_1} \rangle (e_{k_1})_{\alpha_1}$, arising as a matrix element of the vector potential operator. Under H, T and HT the part $\phi_1 (e_{k_1})_{\alpha_1}$ becomes

$$\left(\phi_1^* (e_{k_1}^*)_{\alpha_1}\right)^* \quad - \phi_2 \left(\phi_1 (e_{\bar{k}_1})_{\alpha_1}\right)^* \quad - \phi_2 \left(\phi_1^* (e_{\bar{k}_1}^*)_{\alpha_1}\right) \quad (3.46)$$

respectively. As in §3.1.2, if k_1 involves emission then ϕ_2^* replaces ϕ_2 . Thus under

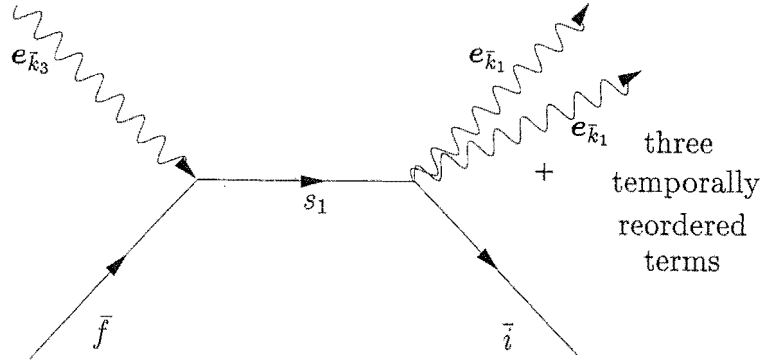


Fig. 3.13: HT symmetry as applied to the quadratic terms in the second-harmonic generation amplitude (compare with Fig. 3.10). The resulting expressions correspond to the quadratic terms for parametric down-conversion. The temporal ordering shown is for photon 3 absorbed and 1 and 2 emitted, this corresponds to the first term in Eq.(3.43) (i.e. HT symmetry applied to the diagram shown in Fig. 3.10).

H, T and HT the photon parts transform to

$$\gamma_{\{\alpha\};\text{Coul}}^{\{n_k n'_k\}} \quad (-1)^N \phi_2^Z \gamma_{\{\alpha\};\text{Coul}}^{\{n'_k n_k\}} \quad (-1)^N \phi_2^Z \gamma_{\{\alpha\};\text{Coul}}^{\{n_k n'_k\}} \quad (3.47)$$

respectively. Together Eqs.(3.45) and (3.47) show that the reversality theorems in the Coulomb gauge are identical to those in the multipolar gauge (Eqs.(3.25) to (3.27)).

3.2 Symmetrised operators

Thus far time reversal symmetry has been defined and applied to the transition amplitude of a general nonlinear optical process. Our contribution has been to include in the H, T and HT relations the phenomenological damping factors Γ (and to allow for arbitrary phase choices in Eq.(3.21)). Before moving on to examine the consequences that follow from these reversality theorems, we define an effective transition operator, and symmetrised versions thereof, that will be useful in latter analyses for stating some general results (§3.3 and Chap. 7), and deriving practical selection rules for nonlinear optic coefficients in or near the nonresonant limit (Chap. 4).

The HT signature $\tau_{\mathcal{O}}$ of an operator \mathcal{O} is defined by

$$\bar{\mathcal{O}}^\dagger = \tau_{\mathcal{O}} \mathcal{O}. \quad (3.48)$$

We define an effective transition operator $O_{\{\mathbf{k}\}}^{\{\alpha, \eta\}}$ through the relation

$$\langle f | O_{\{\mathbf{k}\}}^{\{\alpha, \eta\}} | i \rangle = O_{fi\{\mathbf{k}\}}^{\{\alpha, \eta\}}, \quad (3.49)$$

so that the matrix element of $O_{\{\mathbf{k}\}}^{\{\alpha,\eta\}}$ between the final and initial electronic states gives the electronic parts of the transition amplitude; its form follows directly from Eq.(2.16). From Eq.(3.13)

$$\left(O_{\{\mathbf{k}\}}^{\{\alpha,\eta\}}\right)^\dagger = O_{\{-\mathbf{k}\}}^{\{\alpha,-\eta\}}, \quad (3.50)$$

i.e. the operator does not have a definite HT signature. In particular, the energy denominators of the effective transition operator differ between a given process and its time reversal conjugate (the $\{\eta\}$ are of opposite sign); the wavevectors in the numerator are also opposite. To overcome this we separate this operator into parts which are symmetric and antisymmetric under HT:

$$O_{\{\mathbf{k}\}\pm}^{\{\alpha,\eta\}} \equiv \frac{1}{2} \left(O_{\{\mathbf{k}\}}^{\{\alpha,\eta\}} \pm O_{\{-\mathbf{k}\}}^{\{\alpha,-\eta\}} \right). \quad (3.51)$$

Each of the symmetrised parts $O_{\{\mathbf{k}\}\pm}^{\{\alpha,\eta\}}$ has a definite HT signature:

$$\left(O_{\{\mathbf{k}\}\pm}^{\{\alpha,\eta\}}\right)^\dagger = \pm O_{\{\mathbf{k}\}\pm}^{\{\alpha,\eta\}}, \quad (3.52)$$

and together sum to give the physical operator:

$$O_{\{\mathbf{k}\}}^{\{\alpha,\eta\}} = O_{\{\mathbf{k}\}+}^{\{\alpha,\eta\}} + O_{\{\mathbf{k}\}-}^{\{\alpha,\eta\}}. \quad (3.53)$$

When attention is restricted to Rayleigh and Raman scattering in the electric dipole approximation, the introduction of HT-symmetrized operators has much in common with the discussion of Barron and Nørby Svendsen [15]. Hecht and Barron [61], in analysing various forms of optical activity in Rayleigh and Raman scattering, also consider symmetrized operators but with magnetic dipole and electric quadrupole terms also included. Equation (3.51) includes all multipole terms and shall be employed in discussing parametric nonlinear optical processes.

The light scattering intensity for coherent processes, $I_{\text{coh}}^{\{n'_k n_k\}}$ (Eq.(2.12)), is proportional to the modulus-squared of

$$\sum_{\{\alpha\}} \gamma_{\{\alpha\}}^{\{n'_k n_k\}} \sum_i M_i O_{ii\{\mathbf{k}\}}^{\{\alpha,\eta\}}. \quad (3.54)$$

In §2.3.2, when deriving the form of $I_{\text{coh}}^{\{n'_k n_k\}}$, we placed no restriction on the relative values of the M_i (the occupation numbers of the various one particle states, i , initially populated by the electronic subsystem). For the remainder of this thesis we shall suppose that for every state i that is occupied, its T-conjugate \bar{i} is equally occupied, i.e.

$$M_{\bar{i}} = M_i. \quad (3.55)$$

For this situation we denote the $\sum_i M_i$ as Av_i , which we term a statistical population average (over i).

We now have

$$\begin{aligned} \text{Av}_i O_{ii\{\mathbf{k}\}}^{\{\alpha,\eta\}} &= \text{Av}_i \left(O_{ii\{\mathbf{k}\}+}^{\{\alpha,\eta\}} + O_{ii\{\mathbf{k}\}-}^{\{\alpha,\eta\}} \right) = \text{Av}_i \left(O_{ii\{\mathbf{k}\}+}^{\{\alpha,\eta\}} - O_{ii\{\mathbf{k}\}-}^{\{\alpha,\eta\}} \right) \\ &= \text{Av}_i O_{ii\{\mathbf{k}\}+}^{\{\alpha,\eta\}}, \end{aligned} \quad (3.56)$$

so that intensity involves only the symmetric part:

$$I_{\text{coh}}^{\{n'_k n_k\}} = \frac{2\pi}{\hbar} \left| \sum_{\{\alpha\}} \gamma_{\{\alpha\}}^{\{n'_k n_k\}} \text{Av}_i O_{ii\{\mathbf{k}\}+}^{\{\alpha,\eta\}} \right|^2 \delta(E_{\{n_k\}} - E_{\{n'_k\}}). \quad (3.57)$$

The electronic parts of the amplitude are now invariant under the combined operations of $\{\eta\} \rightarrow \{-\eta\}$ and $\{\mathbf{k}\} \rightarrow \{-\mathbf{k}\}$. For coherent processes the use of these symmetrized operators therefore simplifies the coherence relation between interference terms within a degenerate space if a statistical average is required.

From Eq.(3.10) \bar{i} and i are degenerate, therefore Av_i places a restriction on the way in which degenerate levels may be populated. This average is satisfied if, for example, each state within a degenerate electronic energy level E_i is equally populated:

$$\text{Av}_i = \sum_i M(E_i), \quad (3.58)$$

i.e. the occupation number is a function only of the energy and the sum runs over all states within each level that is occupied. The average would, in general, be invalidated by a population imbalance from polarised pumping. It is assumed to be valid in the cases we consider, and covers the case where a thermal average is required (where $M(E_i)$ is proportional to $e^{-E_i/kT}$).

3.3 Nonlinear optical Onsager relations

3.3.1 Onsager relations and polarisation symmetries

Onsager derived reciprocal relations on transport coefficients by incorporating microscopic reversibility into a statistical mechanical treatment of irreversible linear processes [109, 110]. The optical analogue is the symmetry

$$\varepsilon_{\alpha_1 \alpha_2}(\omega, \mathbf{k}) = \varepsilon_{\alpha_2 \alpha_1}(\omega, -\mathbf{k}) \quad (3.59)$$

on the Cartesian components of the dielectric tensor ε (e.g. Shelankov and Pikus [120], Etchegoin *et al.* [38]). Although nonlinear Onsager relations have been discussed in contexts such as nucleation [123], relations applicable to nonlinear optical tensors have not yet been formulated. We present here Onsager relations specific to a restricted class of coherent processes. Our derivation is based on

Eq.(3.57); although it is not discussed here, equivalent results may also be derived on the relevant correlation functions (e.g. Mahan [96]; see also Krempasky and Schmid [78]).

HT symmetry relates amplitudes for processes where the in and out states are interchanged and time reversed (Eq.(3.27)). In general such HT-conjugate processes bear little direct resemblance to one another. However, if attention is restricted to processes where for each input photon there is an output photon of identical energy and vice versa, this is no longer the case. In particular, because HT interchanges in and out photons, and because each input photon can be grouped with one output photon of identical energy, this interchange results in a process that is of the same type as the original (Fig. 3.14). We term such processes self-conjugate.

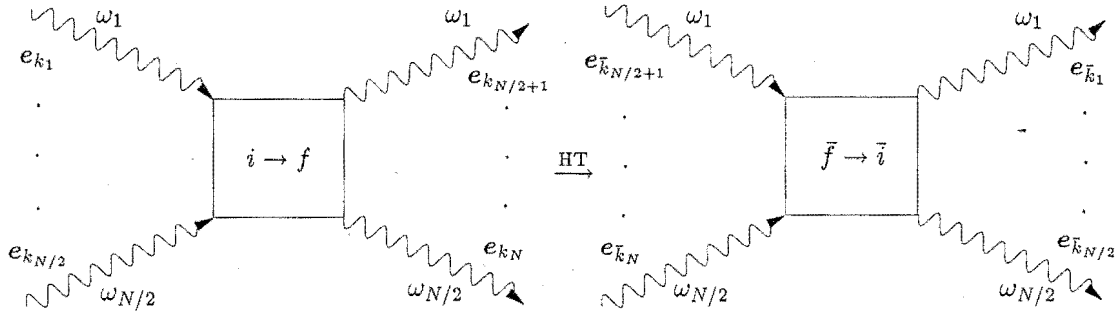


Fig. 3.14: This figure represents Figs. 2.3 and 3.3 when attention is restricted to self-conjugate processes. Because the input and output photons form degenerate pairs, HT symmetry applied to a self-conjugate process results in a self-conjugate process of the same type.

We show that for self-conjugate processes the effect of HT on the electronic parts is to interchange the polarisation labels and interchange and reverse the wavevectors within each degenerate pair of photons (as well as interchanging and time reversing the initial and final electronic states). We denote these interchanges by the permutation π_s . As shown in Fig. 3.14, we number the photons such that photon p and $p + N/2$ have the same energy ($p \leq N/2$), so that

$$\pi_s(\alpha_p, \eta_p, \mathbf{k}_p; \alpha_{p+N/2}, \eta_{p+N/2}, \mathbf{k}_{p+N/2}) = (\alpha_{p+N/2}, -\eta_{p+N/2}, -\mathbf{k}_{p+N/2}; \alpha_p, -\eta_p, -\mathbf{k}_p). \quad (3.60)$$

Note, because $\eta_p = -\eta_{p+N/2}$ the permutation has no effect on those labels, i.e. $\pi_s\{\eta\} = \{\eta\}$.

For self-conjugate processes the numerator and denominator parts of the amplitude satisfy

$$N_{ii\{-\mathbf{k}\}}^{\{\alpha, -\eta\}\{s\}} = N_{ii\pi_s v\{\mathbf{k}\}}^{\pi_s v\{\alpha, \eta\}\{s\}}, \quad (3.61)$$

$$D_{ii}^{\{-\eta\}\{s\}} = D_{ii}^{v\{\eta\}\{s\}} \quad (3.62)$$

(these relations are most readily understood by considering the examples in §3.3.2). In a similar vein as in Eq.(3.4) we have defined a reordering operation v which acts on the labels $\{\alpha, \eta, \mathbf{k}\}$ so as to transform the contribution associated with one temporal ordering of the photon interactions into the contribution from another temporal ordering. In particular, for a given ordering of those labels v swaps each photon p with photon $p + N/2$ ($p \leq N/2$). For example, under v the ordering $N, \dots, 1$ becomes the ordering $N/2, \dots, 1, N, \dots, N/2 + 1$. Together, Eqs. (3.61) and (3.62) show the amplitude is invariant under π_s :

$$\begin{aligned}
 \text{Av}_i O_{ii\{\mathbf{k}\}}^{\{\alpha, \eta\}} &= \text{Av}_i \sum_{\pi\{\alpha\}, \{s\}} \frac{N_{ii\{-\mathbf{k}\}}^{\pi\{\alpha, -\eta\}\{s\}}}{D_{ii}^{\pi\{-\eta\}\{s\}}} \\
 &= \text{Av}_i \sum_{\pi\{\alpha\}, \{s\}} \frac{N_{ii\pi\{\pi_s v\{\mathbf{k}\}\}}^{\pi\{\pi_s v\{\alpha, \eta\}\}\{s\}}}{D_{ii}^{\pi\{\pi_s v\{\eta\}\}\{s\}}} \\
 &= \text{Av}_i \sum_{\pi\{\alpha\}, \{s\}} \frac{N_{ii\pi\{\pi_s\{\mathbf{k}\}\}}^{\pi\{\pi_s\{\alpha, \eta\}\}\{s\}}}{D_{ii}^{\pi\{\pi_s\{\eta\}\}\{s\}}} \\
 &= \text{Av}_i O_{ii\pi_s\{\mathbf{k}\}}^{\pi_s\{\alpha, \eta\}}, \tag{3.63}
 \end{aligned}$$

where the first step follows from Eq.(3.57), the second from Eqs.(3.61) and (3.62), and the third because of the sum over temporal orderings $\pi\{\alpha\}$. Equation (3.63) is therefore a special case of the general condition that the electronic parts of two HT-conjugate amplitudes must be equivalent.

The lowest order self-conjugate process is coherent Rayleigh scattering ($N=2$), and for this process Eq.(3.63) reduces to the optical Onsager relation given in Eq.(3.59) (see also Eq.(3.66)). However, Eq.(3.63) also gives such index symmetries for higher order self-conjugate processes (see for example Eq.(3.70)), and for this reason may be considered a nonlinear optical Onsager relation.

In the electric dipole approximation the reversal of the wavevectors has no effect and Eq.(3.63) reduces to the symmetry of interchanging all the polarisation label pairs: $\alpha_p \leftrightarrow \alpha_{p+N/2}$. Loudon [92, 93], Barron and Nørby Svendsen [15] and Churcher and Stedman [31] treat successfully, and in detail, such relationships between index symmetries and HT symmetry in the context of Rayleigh (and Raman) scattering. For example, the Rayleigh scattering amplitude is invariant with respect to the interchange of the incoming and outgoing polarisation labels.

Equation (3.63) is applicable to non-self-conjugate processes if approximate polarisation label symmetries are considered. The above authors examine Raman scattering where the input and output photon energies are almost degenerate; Barron and Meehan [14] investigate this experimentally. This approximation may be generalised to higher order processes ($N \geq 4$), and the accuracy to which Eq.(3.63) holds will directly reflect the accuracy to which the input and output pairs are degenerate. (Note, near the nonresonant limit approximate polarisation label symmetries may be derived for general coherent nonlinear optical processes as discussed in §4.3.3.)

3.3.2 Examples

In the case of coherent Rayleigh scattering ($\mathbf{k}_1 = \mathbf{k}_2$) the reordering transformation v acts (on the electronic parts) so as to interchange the two contributing temporal orderings:

$$\frac{N_{ii v(\mathbf{k}_1 \mathbf{k}_1)}^{v(\alpha_1 \alpha_2, \eta_1 \eta_2), s_1}}{D_{ii}^{v(\eta_1 \eta_2), s_1}} + \frac{N_{ii v(\mathbf{k}_1 \mathbf{k}_1)}^{v(\alpha_2 \alpha_1, \eta_2 \eta_1), s_1}}{D_{ii}^{v(\eta_2 \eta_1), s_1}} = \frac{N_{ii \mathbf{k}_1 \mathbf{k}_1}^{\alpha_2 \alpha_1, \eta_2 \eta_1, s_1}}{D_{ii}^{\eta_2 \eta_1, s_1}} + \frac{N_{ii \mathbf{k}_1 \mathbf{k}_1}^{\alpha_1 \alpha_2, \eta_1 \eta_2, s_1}}{D_{ii}^{\eta_1 \eta_2, s_1}}. \quad (3.64)$$

The effect of π_s on the right hand side of this equation gives

$$\frac{N_{ii \pi_s \{\mathbf{k}_1 \mathbf{k}_1\}}^{\pi_s \{\alpha_2 \alpha_1, \eta_2 \eta_1\}, s_1}}{D_{ii}^{\pi_s \{\eta_2 \eta_1\}, s_1}} + \frac{N_{ii \pi_s \{\mathbf{k}_1 \mathbf{k}_1\}}^{\pi_s \{\alpha_1 \alpha_2, \eta_1 \eta_2\}, s_1}}{D_{ii}^{\pi_s \{\eta_1 \eta_2\}, s_1}} = \frac{N_{ii -\mathbf{k}_1 -\mathbf{k}_1}^{\alpha_1 \alpha_2, -\eta_1 -\eta_2, s_1}}{D_{ii}^{-\eta_1 -\eta_2, s_1}} + \frac{N_{ii -\mathbf{k}_1 -\mathbf{k}_1}^{\alpha_2 \alpha_1, -\eta_2 -\eta_1, s_1}}{D_{ii}^{-\eta_2 -\eta_1, s_1}}, \quad (3.65)$$

verifying Eqs.(3.61) and (3.62) for $N=2$. Hence,

$$\text{Av}_i O_{ii \mathbf{k}_1 \mathbf{k}_1}^{\alpha_1 \alpha_2, \eta_1 \eta_2} = \text{Av}_i O_{ii -\mathbf{k}_1 -\mathbf{k}_1}^{\alpha_2 \alpha_1, \eta_1 \eta_2}, \quad (3.66)$$

i.e. the electronic parts are invariant under the combined interchanges $\alpha_1 \leftrightarrow \alpha_2$, $\mathbf{k}_1 \rightarrow -\mathbf{k}_1$. Equation (3.66) may of course also be derived from first principles by applying HT symmetry to the electronic parts of the coherent Rayleigh scattering amplitude when a statistical average is required (Eq.(3.33) in the case where $f = i$ and Av_i is present).

The next order self-conjugate process is the four-wave mixing process ($N=4$) in which photons ω_1, \mathbf{k}_1 and ω_2, \mathbf{k}_2 are absorbed and $\omega_3 = \omega_1, \mathbf{k}_3$ and $\omega_4 = \omega_2, \mathbf{k}_4$ emitted (with $\mathbf{k}_1 + \mathbf{k}_2 = \mathbf{k}_3 + \mathbf{k}_4$). There are twenty four possible temporal orderings, for illustrative purposes we consider 1 absorbed, 2 absorbed, 3 emitted, 4 emitted. The numerator and denominator factors for this ordering are

$$\frac{N_{ii \mathbf{k}_1 \mathbf{k}_2 \mathbf{k}_3 \mathbf{k}_4}^{\alpha_1 \alpha_2 \alpha_3 \alpha_4, \eta_1 \eta_2 \eta_3 \eta_4, s_3 s_2 s_1}}{D_{ii}^{\eta_1 \eta_2 \eta_3 \eta_4, s_3 s_2 s_1}} = \frac{\langle i | \xi_{\alpha_4}^{+, \mathbf{k}_4} | s_3 \rangle \langle s_3 | \xi_{\alpha_3}^{+, \mathbf{k}_3} | s_2 \rangle \langle s_2 | \xi_{\alpha_2}^{-, \mathbf{k}_2} | s_1 \rangle \langle s_1 | \xi_{\alpha_1}^{-, \mathbf{k}_1} | i \rangle}{(E_{i, s_1} + \hbar \omega_1 + i \Gamma_{s_1}) (E_{i, s_2} + \hbar \omega_1 + \hbar \omega_2 + i \Gamma_{s_2}) (E_{i, s_3} + \hbar \omega_2 + i \Gamma_{s_3})}. \quad (3.67)$$

Under v this transforms into the term

$$\frac{N_{ii v(\mathbf{k}_1 \mathbf{k}_2 \mathbf{k}_3 \mathbf{k}_4)}^{v(\alpha_1 \alpha_2 \alpha_3 \alpha_4, \eta_1 \eta_2 \eta_3 \eta_4), s_3 s_2 s_1}}{D_{ii}^{v(\eta_1 \eta_2 \eta_3 \eta_4), s_3 s_2 s_1}} = \frac{\langle i | \xi_{\alpha_2}^{-, \mathbf{k}_2} | s_3 \rangle \langle s_3 | \xi_{\alpha_1}^{-, \mathbf{k}_1} | s_2 \rangle \langle s_2 | \xi_{\alpha_4}^{+, \mathbf{k}_4} | s_1 \rangle \langle s_1 | \xi_{\alpha_3}^{+, \mathbf{k}_3} | i \rangle}{(E_{i, s_1} - \hbar \omega_1 + i \Gamma_{s_1}) (E_{i, s_2} - \hbar \omega_1 - \hbar \omega_2 + i \Gamma_{s_2}) (E_{i, s_3} - \hbar \omega_2 + i \Gamma_{s_3})} = \frac{N_{ii \mathbf{k}_3 \mathbf{k}_4 \mathbf{k}_1 \mathbf{k}_2}^{\alpha_3 \alpha_4 \alpha_1 \alpha_2, \eta_3 \eta_4 \eta_1 \eta_2, s_3 s_2 s_1}}{D_{ii}^{\eta_3 \eta_4 \eta_1 \eta_2, s_3 s_2 s_1}}, \quad (3.68)$$

corresponding to the ordering 3 emitted, 4 emitted, 1 absorbed, 2 absorbed. Under π_s this becomes

$$\begin{aligned} & \frac{N_{ii}^{\pi_s \{ \alpha_3 \alpha_4 \alpha_1 \alpha_2, \eta_3 \eta_4 \eta_1 \eta_2 \}, s_3 s_2 s_1}}{D_{ii}^{\pi_s \{ \eta_3 \eta_4 \eta_1 \eta_2 \}, s_3 s_2 s_1}} = \\ & \frac{\langle i | \xi_{\alpha_4}^{-, -\mathbf{k}_4} | s_3 \rangle \langle s_3 | \xi_{\alpha_3}^{-, -\mathbf{k}_3} | s_2 \rangle \langle s_2 | \xi_{\alpha_2}^{+, -\mathbf{k}_2} | s_1 \rangle \langle s_1 | \xi_{\alpha_1}^{+, -\mathbf{k}_1} | i \rangle}{(E_{i, s_1} - \hbar\omega_1 + i\Gamma_{s_1}) (E_{i, s_2} - \hbar\omega_1 - \hbar\omega_2 + i\Gamma_{s_2}) (E_{i, s_3} - \hbar\omega_2 + i\Gamma_{s_3})} = \\ & \frac{N_{ii}^{\alpha_1 \alpha_2 \alpha_3 \alpha_4, -\eta_1 - \eta_2 - \eta_3 - \eta_4, s_3 s_2 s_1}}{D_{ii}^{-\eta_1 - \eta_2 - \eta_3 - \eta_4, s_3 s_2 s_1}}, \end{aligned} \quad (3.69)$$

verifying Eqs.(3.61) and (3.62) for this ($N=4$) case; similar verifications may be carried out for the other temporal orderings. Equation (3.63) for this process takes the form

$$\text{Av}_i O_{ii \mathbf{k}_1 \mathbf{k}_2 \mathbf{k}_3 \mathbf{k}_4}^{\alpha_1 \alpha_2 \alpha_3 \alpha_4, \eta_1 \eta_2 \eta_3 \eta_4} = \text{Av}_i O_{ii -\mathbf{k}_3 -\mathbf{k}_4 -\mathbf{k}_1 -\mathbf{k}_2}^{\alpha_3 \alpha_4 \alpha_1 \alpha_2, \eta_1 \eta_2 \eta_3 \eta_4}, \quad (3.70)$$

i.e. the electronic parts of the amplitude are invariant under the combined interchanges $\alpha_1, \mathbf{k}_1 \leftrightarrow \alpha_3, -\mathbf{k}_3$ and $\alpha_2, \mathbf{k}_2 \leftrightarrow \alpha_4, -\mathbf{k}_4$.

3.4 Optical rotation in GaAs

Zheludev *et al.* [143] claim there are nonzero terms in the dielectric tensor ϵ appropriate to GaAs and InSb crystals that are linear in the wavevector, where such terms would be forbidden if the Onsager relation (Eq.(3.59)) were to hold. This “time-nonreversible light interaction” is traced to spin-orbit coupling. Their experimental results on the rotation of the plane of polarisation of linearly polarised incident light in normal specular reflection in GaAs and InSb crystals are then attributed, at least in part, as originating from these terms (Zheludev *et al.* [143] and references therein; for a recent reference see Bennett *et al.* [16]).

There is no doubt that new amplitudes can arise when spin-orbit coupling is considered [13, 43, 73], for example matrix elements between T-conjugate states in Kramers systems are then nonzero (see §4.3.2). However, the claim of Zheludev *et al.* [143] is discredited by the following consideration: The spin-orbit interaction neither has time-odd parts nor affects statistical averages, and hence cannot affect the validity of the Onsager relation. This point is made by Etchegoin *et al.* [38] and supported by them using a microscopic analysis of the Onsager relation for the dielectric tensor appropriate to the electronic band structure of GaAs. These criticisms were amplified in Lew Yan Voon *et al.* [90] but were totally rejected in Zheludev *et al.* [142]. Zheludev *et al.* [142] noted that in their experiment Etchegoin *et al.* [38] consider induced ellipticity of linearly polarised incident light in transmission rather than the rotation of the plane of polarisation in normal specular reflection, but failed to adequately address the microscopic proof of Etchegoin *et al.* [38]. Both agree that the Onsager relation may be violated in

the high excitation case (pump-induced case) which renders statistical averaging inappropriate.

The microscopic expressions quoted in Zheludev *et al.* [143] for the terms in the dielectric tensor that violate the Onsager relation were originally derived in Bungay *et al.* [22], in which rotation of the plane of polarisation in transmission is also considered. The results of §3.3.1 prove in general that if a statistical average is present the Onsager relations applicable to self-conjugate processes are valid regardless of the presence of spin-orbit coupling. This confirms the criticisms in Etchegoin *et al.* [38] and Lew Yan Voon *et al.* [90] of Zheludev *et al.* [143] and extends their analysis to allow for the possibility of intermediate resonances. We are able to verify here that both the rotation of the plane of polarisation and induced ellipticity are forbidden up to first order in the photon wavevector for electronic subsystems possessing T_d symmetry. Based on this analysis we correct Bungay *et al.* [22], who relate their Onsager-forbidden terms directly to the spin-orbit interaction.

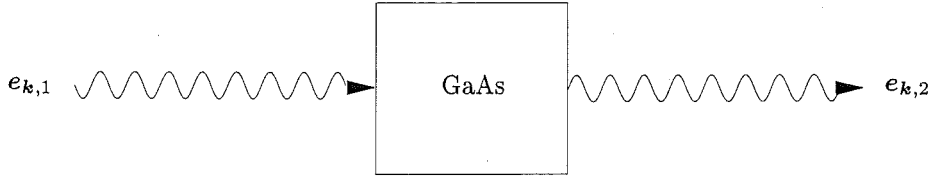


Fig. 3.15: One of the processes considered in Bungay *et al.* [22]: Light of linear polarisation $e_{k,1}$ is passed through a GaAs crystal and the rate of production of $e_{k,2}$ is measured, where $e_{k,2}$ is orthogonal to $e_{k,1}$.

Optical rotation in transmission may be modelled as the coherent process of forward Rayleigh scattering between orthogonal linear polarisations $e_{k,1}$ and $e_{k,2}$ (both with wavevector \mathbf{k}) [57, 113]. The associated Onsager relation for this self-conjugate process is given by Eq.(3.59), or Eq.(3.66) in our notation. Following Etchegoin *et al.* [38] we expand Eq.(3.66) in powers of the wavevector:

$$\text{Av}_i O_{ii\mathbf{k}\mathbf{k}}^{\alpha_1\alpha_2,\eta_1\eta_2} = \text{Av}_i O_{ii\{0\}}^{\alpha_1\alpha_2} + \text{Av}_i O_{ii\alpha}^{\alpha_1\alpha_2}(\mathbf{k})_\alpha + \dots, \quad (3.71)$$

where we suppress the $\{\eta\}$ labels, the subscript $\{0\}$ indicates the electric dipole approximation and

$$\text{Av}_i O_{ii\alpha}^{\alpha_1\alpha_2} \equiv \frac{\partial}{\partial(\mathbf{k})_\alpha} \text{Av}_i O_{ii\mathbf{k}\mathbf{k}}^{\alpha_1\alpha_2,\eta_1\eta_2} \Big|_{\mathbf{k}=0}. \quad (3.72)$$

From Eq.(3.66)

$$\text{Av}_i O_{ii\{0\}}^{\alpha_1\alpha_2} = \text{Av}_i O_{ii\{0\}}^{\alpha_2\alpha_1} \quad \text{Av}_i O_{ii\alpha}^{\alpha_1\alpha_2} = - \text{Av}_i O_{ii\alpha}^{\alpha_2\alpha_1}. \quad (3.73)$$

The T_d symmetry restrictions require $\text{Av}_i O_{ii\{0\}}^{\alpha_1\alpha_2} \propto \delta_{\alpha_1\alpha_2}$ and the nonzero components of $\text{Av}_i O_{ii\alpha}^{\alpha_2\alpha_1}$ to be identical and those with $\alpha_1\alpha_2\alpha$ being a permutation of

xyz (e.g. Butcher and Cotter [23]). This second index symmetry is incompatible with the Onsager constraint. Hence, up to the lowest two orders optical rotation is forbidden:

$$\text{Av}_i O_{ii\{0\}}^{\alpha_1\alpha_2} (e_{k,1})_{\alpha_1} (e_{k,2})_{\alpha_2} \propto e_{k,1} \cdot e_{k,2} = 0 \quad \text{Av}_i O_{ii\alpha}^{\alpha_2\alpha_1} = 0. \quad (3.74)$$

In their equations 7 and 8 Bungay *et al.* [22] give explicit formulae for the parts of $\text{Av}_i O_{ii\{0\}}^{\alpha_1\alpha_2}$ and $\text{Av}_i O_{ii\alpha}^{\alpha_2\alpha_1}$ (ϵ_{ij}^a and γ_{ijl}^s in their notation) that violate Eq.(3.73). Following after their equation 10 it is stated that these expressions are nonzero when spin-orbit coupling is present since the wavefunctions cannot then be chosen as real. Although this final statement in itself is correct, their conclusions are false. The reason for this, and the key reason why their analysis is incomplete, is their *omission* of a statistical (thermal) average. In particular, their formulae lack a sum over the degeneracies found in the initial states (g in their notation, i in ours). This is of importance in deriving the Onsager relations since in general i and \bar{i} are inequivalent. On performing such an average their Onsager-violating terms cancel.

Although the above analysis covers transmission in particular, we expect our conclusion concerning optical rotation to also hold in reflection. Firstly, the reflection and transmission amplitudes found in Bungay *et al.* [22] involve the same bulk susceptibilities (see also Silverman [124]). Secondly, interrelationships between and within reflection and transmission coefficient components may be found using energy conservation (which can also contain phase information [111]). For example, Silverman and Badoz [125] and Lekner [86] relate components in both circular and in mixed circular and linear bases. Incidentally, relations of this type are also of importance in discussions of time reversal violation in high temperature superconductors [56, 82, 88, 120] (see also Stedman *et al.* [131] for a related discussion).

Finally, we note that in certain special cases a statistical average is in fact not required to derive the Onsager relations. In particular, when the Hamiltonian does not contain any spin-dependent terms (such as spin-orbit coupling) and when the spatial parts of the electronic wavefunction can be chosen to be real (i.e. if it is equal to its T-conjugate). For example the right hand side of Eq.(3.33) for $f = i$ is now invariant under $\bar{i} \rightarrow i$ because i and \bar{i} differ only in spin projection. Hence our requirement that Av_i give an equal weighting to i and \bar{i} (Eq.(3.55)) is no longer necessary (because spin is a redundant variable); this point is implicit in the analysis of Landau and Lifshitz [81].

4. The nonresonant limit

In this chapter we discuss selection rules on the electronic parts of the transition amplitude which follow from HT symmetry together with the assumption that the nonresonant limit holds (this limit is defined in §4.1). These rules have not received much attention in the literature (see §4.1) and are significantly different in content from the results discussed in Chap. 3. Certain rules presented in this chapter are applicable to general coherent processes and others to transitions between T-conjugate states (§4.3); in both cases the number of participating photons is arbitrary. We verify that identical results are also found in the Coulomb gauge (§4.4). Such a verification has been previously required for the specific example of Judd-Ofelt theory to settle a major discussion on which spherical rank tensors are needed to describe the associated effective transition operator (see Refs. [114, 137] and also Chap. 7).

4.1 Definition and introduction

By definition, in the nonresonant limit the photon energies, $\hbar\omega_p$, are far removed from the electronic energy differences, $E_{i,s}$, ($\hbar\omega_p \ll E_{i,s}$) and also

$$\hbar\omega \ll E_{i,s} \qquad \hbar\omega \equiv \sum_p \eta_p \hbar\omega_p, \quad (4.1)$$

where $\hbar\omega$ is a generic term denoting any sum of the participating modes (i.e. in the nonresonant limit all the participating photons are substantially off-resonant). Following directly from Eqs.(2.18) and (4.1), the energy denominators of the transition amplitude now take the simplified form

$$D_{fi}^{\{\eta\}\{s\}} \rightarrow (E_{i,s_1})(E_{i,s_2}) \dots (E_{i,s_{N-1}}) \equiv D_{fi}^{\{0\}\{s\}}; \quad (4.2)$$

the damping factors, Γ_s , may of course be ignored in this limit. Thus, the denominators corresponding to each possible temporal ordering are identical:

$$D_{fi}^{\pi\{0\}\{s\}} = D_{fi}^{\{0\}\{s\}}. \quad (4.3)$$

Equation (4.3) simplifies the index symmetries of the electronic parts of the transition amplitude, and in the electric dipole approximation results in the amplitude

being totally symmetric under the interchange of any of the Cartesian labels $\{\alpha\}$ (e.g. Ref. [23]). In our notation this may be seen as follows:

$$O_{fi\{0\}}^{\{\alpha,0\}} = \sum_{\{s\}} \frac{\sum_{\pi\{\alpha\}} N_{fi\{0\}}^{\pi\{\alpha,0\}\{s\}}}{D_{fi}^{\{0\}\{s\}}}, \quad (4.4)$$

so for some permutation π' of the labels we have

$$O_{fi\{0\}}^{\pi'\{\alpha,0\}} = \sum_{\{s\}} \frac{\sum_{\pi\{\alpha\}} N_{fi\{0\}}^{\pi'\{\pi\{\alpha,0\}\}\{s\}}}{D_{fi}^{\{0\}\{s\}}} = \sum_{\{s\}} \frac{\sum_{\pi\{\alpha\}} N_{fi\{0\}}^{\pi\{\alpha,0\}\{s\}}}{D_{fi}^{\{0\}\{s\}}} = O_{fi\{0\}}^{\{\alpha,0\}}, \quad (4.5)$$

using the sum over permutations. We have replaced the $\{\eta\}$ by $\{0\}$ in Eq.(4.4) because when both the electric dipole approximation and the nonresonant limit are valid, the amplitude is then independent of whether the participating photons are emitted or absorbed. This symmetry, referred to as Kleinman symmetry, was originally derived by Kleinman [76] as a macroscopic property of crystals using thermodynamic arguments. Equation (4.5) is the key property that follows from taking the nonresonant limit.

Here we discuss how Eqs.(4.3) and (4.5) may be combined with HT symmetry to give selection rules in or near the nonresonant limit. For example, we find that transitions between T-conjugate states in Kramers systems are suppressed in the electric dipole approximation. As described below, such rules have been examined previously by Barron and Nørby Svendsen [15] and Stedman [127] in the case of Rayleigh scattering and mentioned by Kauranen *et al.* [75] for second-harmonic generation. We also extend the discussion of Levine [89] in examining the deviation from Kleinman symmetry in regions slightly outside the nonresonant limit. Finally, we show that identical rules are also found when working in the Coulomb gauge, although the results follow less directly.

4.2 Notation

In §3.1.1, when applying time reversal symmetry to the electronic parts of the transition amplitude, a notation was given that clearly illustrated the physical content of the reversality theorems (§3.1.3). Further, that notation is compact in that all multipole levels are treated together. However, the various HT signatures of the interaction operators are not made explicit but are subsumed into the $\{\mathbf{k}, \eta\} \rightarrow \{-\mathbf{k}, -\eta\}$ notation. In deriving time reversal selection rules in the nonresonant limit, we shall find it useful to make those signatures explicit (for reasons described below), and we shall therefore slightly modify the original notation for the purposes of this chapter. In §4.2.1 we give this modification and the form of the reversal theorem in this modified notation. In preparation for §4.3, we discuss in §4.2.2 the standard lowest order multipole contributions to the transition amplitude, i.e. those involving the electric dipole, magnetic dipole and electric quadrupole interactions.

4.2.1 Reversal theorem

The basic strategy in deriving selection rules is to show that a given contribution to the electronic parts of the transition amplitude is equal to its negative. For this reason the HT symmetry relation on the interaction Hamiltonian as given in Eq.(3.3) is not ideal, and is more usefully written in a modified form. In particular, the right hand side of the final relation in Eq.(3.3) involves the labels $-\mathbf{k}, -\eta$ instead of \mathbf{k}, η . To overcome this we divide the interaction Hamiltonian into two terms:

$$\xi_{\alpha}^{\eta, \mathbf{k}} = \Lambda_{\alpha}^{\eta, \mathbf{k}} + \Upsilon_{\alpha}^{\eta, \mathbf{k}}. \quad (4.6)$$

The first term, $\Lambda_{\alpha}^{\eta, \mathbf{k}}$, is the part of $\xi_{\alpha}^{\eta, \mathbf{k}}$ that involves the interaction with the electric field, namely the first line of Eq.(2.22):

$$\Lambda_{\alpha}^{\eta, \mathbf{k}} = \sum_{\beta} - \int_0^1 du q_{\beta} e^{-iu\eta\mathbf{k} \cdot \mathbf{r}_{\beta}} \mathbf{r}_{\beta}. \quad (4.7)$$

The second term, $\Upsilon_{\alpha}^{\eta, \mathbf{k}}$, is the part of $\xi_{\alpha}^{\eta, \mathbf{k}}$ that involves the interaction with the magnetic field, namely the second and third lines of Eq.(2.22):

$$\begin{aligned} \Upsilon_{\alpha}^{\eta, \mathbf{k}} = & \sum_{\beta} - \int_0^1 \frac{du q_{\beta} u}{2m_{\beta} c} \left\{ \left(((\mathbf{r}_{\beta} \times \mathbf{p}_{\beta}) e^{-iu\eta\mathbf{k} \cdot \mathbf{r}_{\beta}} + e^{-iu\eta\mathbf{k} \cdot \mathbf{r}_{\beta}} (\mathbf{r}_{\beta} \times \mathbf{p}_{\beta})) \times \hat{\mathbf{k}} \right)_{\alpha} \right. \\ & \left. - \frac{q_{\beta}}{c^2} e^{-iu\eta\mathbf{k} \cdot \mathbf{r}_{\beta}} \left(\hat{\mathbf{k}} \cdot \mathbf{r}_{\beta} (\mathbf{s}_{\beta} \times \mathbf{E}_C(\mathbf{r}_{\beta}))_{\alpha} - (\mathbf{s}_{\beta} \times \mathbf{E}_C(\mathbf{r}_{\beta})) \cdot \hat{\mathbf{k}} (\mathbf{r}_{\beta})_{\alpha} \right) \right\}. \end{aligned} \quad (4.8)$$

Because the position operator has an HT signature of +1 and the momentum and spin operators have an HT signature of -1, the last relation in Eq.(3.3) may then be re-expressed as

$$\left(\overline{\Lambda_{\alpha}^{\eta, \mathbf{k}}} \right)^{\dagger} = \Lambda_{\alpha}^{\eta, \mathbf{k}} \quad \left(\overline{\Upsilon_{\alpha}^{\eta, \mathbf{k}}} \right)^{\dagger} = -\Upsilon_{\alpha}^{\eta, \mathbf{k}}. \quad (4.9)$$

As mentioned, we do not have $-\mathbf{k}, -\eta$ labels as in Eq.(3.3) but instead have \mathbf{k}, η on both sides of Eq.(4.9), thus making the time-odd parts explicit rather than subsuming them into the $\{\mathbf{k}, \eta\} \rightarrow \{-\mathbf{k}, -\eta\}$ notation.

Because the interaction Hamiltonian has been divided into two parts, the numerator factor of the transition amplitude may be expressed as a sum of contributions. We define $N_{fi\{\mathbf{k}\};b}^{\{\alpha, \eta\}\{s\}}$ in the same fashion as in Eq.(2.17) but with b of the N matrix elements involving $\Upsilon_{\alpha}^{\eta, \mathbf{k}}$ and $N - b$ involving $\Lambda_{\alpha}^{\eta, \mathbf{k}}$, so that

$$N_{fi\{\mathbf{k}\}}^{\{\alpha, \eta\}\{s\}} = \sum_{b=0}^N N_{fi\{\mathbf{k}\};b}^{\{\alpha, \eta\}\{s\}}. \quad (4.10)$$

Following from Eqs.(3.6) and (4.9), the application of HT symmetry to this gives

$$N_{fi\{\mathbf{k}\};b}^{\{\alpha, \eta\}\{s\}} = (-1)^b N_{i\bar{f}r\{\mathbf{k}\};b}^{r\{\alpha, \eta\}\{\rho(\bar{s})\}}. \quad (4.11)$$

Therefore, by defining

$$O_{fi\{\mathbf{k}\};b}^{\{\alpha,\eta\}} \equiv \sum_{\pi\{\alpha\},\{s\}} \frac{N_{fi\pi\{\mathbf{k}\};b}^{\pi\{\alpha,\eta\}\{s\}}}{D_{fi}^{\pi\{\eta\}\{s\}}}, \quad (4.12)$$

we may rewrite the reversal theorem as

$$O_{fi\{\mathbf{k}\};b}^{\{\alpha,\eta\}} = (-1)^b \sum_{\pi\{\alpha\},\{s\}} \frac{N_{if\pi\{\mathbf{k}\};b}^{\pi\{\alpha,\eta\}\{s\}}}{D_{if}^{\pi\{-\eta\}\{s\}}}. \quad (4.13)$$

Finally, for use in §4.3, we define the parts, $O_{\{\mathbf{k}\};b}^{\{\alpha,\eta\}}$, of the effective transition operator via Eq.(4.12):

$$\langle f | O_{\{\mathbf{k}\};b}^{\{\alpha,\eta\}} | i \rangle = O_{fi\{\mathbf{k}\};b}^{\{\alpha,\eta\}}, \quad (4.14)$$

and symmetrised versions thereof:

$$O_{\{\mathbf{k}\}\pm;b}^{\{\alpha,\eta\}} \equiv \frac{1}{2} \left(O_{\{\mathbf{k}\};b}^{\{\alpha,\eta\}} \pm \left(O_{\{\mathbf{k}\};b}^{\{\alpha,\eta\}} \right)^\dagger \right), \quad (4.15)$$

so that by Eqs.(3.49) and (3.51)

$$\sum_{b=0}^N O_{\{\mathbf{k}\};b}^{\{\alpha,\eta\}} = O_{\{\mathbf{k}\}}^{\{\alpha,\eta\}} \quad \sum_{b=0}^N O_{\{\mathbf{k}\}\pm;b}^{\{\alpha,\eta\}} = O_{\{\mathbf{k}\}\pm}^{\{\alpha,\eta\}}. \quad (4.16)$$

4.2.2 Lowest order multipole contributions

The electric dipole (E1), magnetic dipole (M1) and electric quadrupole (E2) parts of the interaction Hamiltonian are

$$\xi_{\alpha}^{\eta,\mathbf{k}} \Big|_{\text{E1}} = \sum_{\beta} -q_{\beta} (\mathbf{r}_{\beta})_{\alpha} \equiv (\boldsymbol{\mu})_{\alpha}, \quad (4.17)$$

$$\xi_{\alpha}^{\eta,\mathbf{k}} \Big|_{\text{M1}} = \sum_{\beta} -\frac{q_{\beta}}{2m_{\beta}c} ((\mathbf{r}_{\beta} \times \mathbf{p}_{\beta}) \times \hat{\mathbf{k}})_{\alpha} \equiv (\mathbf{m})_{\alpha}, \quad (4.18)$$

$$\xi_{\alpha}^{\eta,\mathbf{k}} \Big|_{\text{E2}} = \sum_{\beta} \frac{i\eta q_{\beta}}{2} \mathbf{k} \cdot \mathbf{r}_{\beta} (\mathbf{r}_{\beta})_{\alpha} \equiv (Q)_{\alpha}, \quad (4.19)$$

respectively. The first and last of these are the two lowest order parts of $\Lambda_{\alpha}^{\eta,\mathbf{k}}$ and the second is the lowest order part of $\Upsilon_{\alpha}^{\eta,\mathbf{k}}$. The magnetic dipole and electric quadrupole operators defined here are not written in their standard form because we have not factored out the photon wavevectors. For example, the usual magnetic dipole operator, \mathbf{m}' , takes the form

$$\mathbf{m}' = \sum_{\beta} -\frac{q_{\beta}}{2m_{\beta}} (\mathbf{r}_{\beta} \times \mathbf{p}_{\beta}) \quad \Rightarrow \quad \frac{\mathbf{m}' \times \hat{\mathbf{k}}}{c} = \mathbf{m}. \quad (4.20)$$

As is standard, we define the electric dipole contribution as involving only μ -type interactions, the magnetic dipole contribution as involving $N - 1$ μ -type interactions and one m -type interaction and the electric quadrupole contribution as involving $N - 1$ μ -type interactions and one Q -type interaction. Most applications may be described using only the electric dipole contribution and in almost all other cases the magnetic dipole and electric quadrupole corrections suffice.

The treatment of spin-orbit coupling in a gauge invariant manner (Eq.(2.27)) requires we include in m the lowest order contribution from the second line of Eq.(4.8):

$$\sum_{\beta} \frac{q_{\beta}^2}{4m_{\beta}c^3} \left(\hat{\mathbf{k}} \cdot \mathbf{r}_{\beta} (\mathbf{s}_{\beta} \times \mathbf{E}_C(\mathbf{r}_{\beta}))_{\alpha} - (\mathbf{s}_{\beta} \times \mathbf{E}_C(\mathbf{r}_{\beta})) \cdot \hat{\mathbf{k}} (\mathbf{r}_{\beta})_{\alpha} \right), \quad (4.21)$$

and because this term is also time-odd, its inclusion will not affect the validity of our results. However, since the effect of this term is assumed to be small, and for ease of comparison with standard expressions, it has been suppressed. The role of this spin-dependent light-matter interaction was raised by Wang and Stedman [137], with particular reference to one photon absorption in rare earths. Judd [69], in commenting on that work, noted that in one photon absorption this term cancels with another interaction resulting from the spatial variation of the electromagnetic field (the one photon absorption resonance condition is used to show this). However, this cancellation is not expected to hold for more general processes and in that case a detailed analysis of the importance of such spin-dependent interactions awaits further discussion; see Harris [60] for a first step.

4.3 The nonresonant limit

The form of the reversal theorem in the nonresonant limit is given in §4.3.1. In §4.3.2 we consider the selection rules which follow from this. The behaviour of the rules in regions slightly outside the nonresonant limit is examined in §4.3.3 and examples are given in §4.3.4.

4.3.1 General considerations

In the nonresonant limit, where the energy denominators are independent of the temporal orderings of the photon interactions (Eq.(4.3)), we have

$$O_{fi\{\mathbf{k}\}}^{\{\alpha,\eta\}} = \sum_{\{s\}} \frac{\sum_{\pi\{\alpha\}} N_{fi\pi\{\mathbf{k}\}}^{\pi\{\alpha,\eta\}\{s\}}}{D_{fi}^{\{0\}\{s\}}} + \mathcal{Q} \quad (4.22)$$

instead of Eq.(2.16) (the electric dipole version of this has been given in Eq.(4.4)). The reversal theorem (Eq.(4.13)) therefore takes the simplified form

$$O_{fi\{\mathbf{k}\};b}^{\{\alpha,\eta\}} = (-1)^b O_{if\{\mathbf{k}\};b}^{\{\alpha,\eta\}}. \quad (4.23)$$

As discussed, we have modified the previous notation used in stating this theorem (Eq.(3.13)) so that now the same photon labels (\mathbf{k}, η) occur on both sides of the relation. In order to obtain the definite phase $(-1)^b$, the interaction Hamiltonian has been divided into two parts (Eq.(4.6)) and the number of interactions involving each part has had to be specified (Eq.(4.10)).

Following directly from Eq.(4.23), the parts of the effective transition operator now have a definite HT signature $(-1)^b$:

$$\left(O_{\{\mathbf{k}\};b}^{\{\alpha,\eta\}}\right)^\dagger = (-1)^b O_{\{\mathbf{k}\};b}^{\{\alpha,\eta\}} \quad (4.24)$$

(c.f. Eq.(3.50)). Hence, only the parts with b even are required for $O_{\{\mathbf{k}\}+;b}^{\{\alpha,\eta\}}$, and b odd for $O_{\{\mathbf{k}\}-;b}^{\{\alpha,\eta\}}$:

$$O_{\{\mathbf{k}\}+;b}^{\{\alpha,\eta\}} \Big|_{b \text{ odd}} = 0 \quad O_{\{\mathbf{k}\}-;b}^{\{\alpha,\eta\}} \Big|_{b \text{ even}} = 0. \quad (4.25)$$

The consequences of Eq.(4.25) are examined in §4.3.2, particularly when only the lowest order multipole contributions to the transition amplitude are considered.

4.3.2 Selection rules

For coherent processes only the symmetric part of the effective transition operator is required (Eq.(3.57)) and thus, by Eq.(4.25), only the parts with b even contribute in the nonresonant limit:

$$I_{\text{coh}}^{\{n'_k n_k\}} = \frac{2\pi}{\hbar} \left| \sum_{\{\alpha\}} \gamma_{\{\alpha\}}^{\{n'_k n_k\}} \text{Av}_i \sum_{b \text{ even}} O_{ii\{\mathbf{k}\}+;b}^{\{\alpha,\eta\}} \right|^2 \delta(E_{\{n_k\}} - E_{\{n'_k\}}). \quad (4.26)$$

Because $b = 1$ for the magnetic dipole contribution, these terms are therefore suppressed in the nonresonant limit for coherent processes. The electric quadrupole (and dipole) terms are not suppressed as they involve $b = 0$. This rule is of importance in estimating the relative magnitudes of the magnetic dipole and electric quadrupole corrections to the electric dipole contribution in the nonresonant limit; it is assumed that the magnetic dipole terms are generally an order of magnitude larger (e.g. Cao and Zhu [28]). This generalises the result of Kau-ranen *et al.* [75], who noted that the magnetic dipole terms in second-harmonic generation are suppressed in the nonresonant limit.

As discussed following Eq.(2.1), the action of T^2 may be summarised as

$$T|\bar{i}\rangle = \tau_s|i\rangle, \quad (4.27)$$

where $\tau_s = +1$ for non-Kramers systems (consisting of an even number of electrons), and is -1 for Kramers systems (consisting of an odd number). Using this definition we have

$$\langle \bar{i} | \mathcal{O} | i \rangle = \tau_{\mathcal{O}} \tau_s \langle \bar{i} | \mathcal{O} | i \rangle \quad (4.28)$$

(see Eqs.(3.1) and (3.48)), which has had many useful applications in linear light-matter interactions [1, 83, 103]. Here we consider transitions between the T-conjugate states i, \bar{i} in Kramers systems; this process is parametric but incoherent. From Eq.(4.28)

$$\langle \bar{i} | O_{\{\mathbf{k}\}}^{\{\alpha, \eta\}} | i \rangle = \langle \bar{i} | O_{\{\mathbf{k}\}-}^{\{\alpha, \eta\}} | i \rangle, \quad (4.29)$$

so by Eq.(4.25) in the nonresonant limit only the parts with b odd contribute:

$$\langle \bar{i} | O_{\{\mathbf{k}\}}^{\{\alpha, \eta\}} | i \rangle = \sum_{b \text{ odd}} \langle \bar{i} | O_{\{\mathbf{k}\}-; b}^{\{\alpha, \eta\}} | i \rangle. \quad (4.30)$$

Hence, the electric dipole and quadrupole terms are suppressed in the nonresonant limit, whereas the magnetic dipole terms are not. As in Eq.(4.26), such a rule is of importance in estimating the relative magnitudes of the various contributions in the nonresonant limit. Barron and Nørby Svendsen [15] and Stedman [127] have previously suggested this rule for Rayleigh scattering, and Moore and Stedman [103] have investigated such a rule for processes involving two arbitrary interactions.

To test Eq.(4.30) experimentally, the following two conditions must be satisfied. First, i and \bar{i} must not be degenerate if the effect is not to be masked by other transitions; this requires a time-odd perturbation such as Zeeman splitting. Second, because the spin-dependence of the interaction Hamiltonian is negligible, appreciable spin-orbit mixing of the ground configuration is required in Kramers systems so that T-conjugate states are not orthogonal in spin space.

4.3.3 Regions near the nonresonant limit

The selection rules in §4.3.2 follow from Eq.(4.25) when attention is restricted to coherent processes or transitions between T-conjugate states in Kramers systems. Their derivation involves assuming the nonresonant limit, i.e. that the scaling parameter g , defined as the ratio of the photon energies to the electronic energy differences, is negligible:

$$g \equiv \hbar\omega / E_{i, s_n} \rightarrow 0. \quad (4.31)$$

We now examine the lowest order corrections in g to those rules.

From Eqs.(4.13) and (4.15) we have

$$\langle f | O_{\{\mathbf{k}\} \pm; b}^{\{\alpha, \eta\}} | i \rangle = \sum_{\pi\{\alpha\}, \{s\}} N_{fi\pi\{\mathbf{k}\}; b}^{\pi\{\alpha, \eta\}\{s\}} \left\{ \frac{1}{D_{fi}^{\pi\{\eta\}\{s\}}} \pm \frac{(-1)^b}{D_{fi}^{\pi\{-\eta\}\{s\}}} \right\} = \sum_{\pi\{\alpha\}, \{s\}} \frac{N_{fi\pi\{\mathbf{k}\}; b}^{\pi\{\alpha, \eta\}\{s\}}}{\mathcal{D}_{fi \pm; b}^{\pi\{\eta\}\{s\}}}, \quad (4.32)$$

where

$$\frac{1}{\mathcal{D}_{fi\pm;b}^{\{\eta\}\{s\}}} \equiv \frac{D_{fi}^{\{-\eta\}\{s\}} \pm (-1)^b D_{fi}^{\{\eta\}\{s\}}}{D_{fi}^{\{\eta\}\{s\}} D_{fi}^{\{-\eta\}\{s\}}}. \quad (4.33)$$

For b even $\mathcal{D}_{fi\pm;b}^{\{\eta\}\{s\}} =$

$$\frac{(E_{i,s_1} + \hbar\eta_1\omega_1) \dots (E_{i,s_{N-1}} + \hbar \sum_{p=1}^{N-1} \eta_p\omega_p) \pm (E_{i,s_1} - \hbar\eta_1\omega_1) \dots (E_{i,s_{N-1}} - \hbar \sum_{p=1}^{N-1} \eta_p\omega_p)}{(E_{i,s_1}^2 - (\hbar\eta_1\omega_1)^2) (E_{i,s_2}^2 - (\hbar\eta_1\omega_1 + \hbar\eta_2\omega_2)^2) \dots (E_{i,s_{N-1}}^2 - (\hbar \sum_{p=1}^{N-1} \eta_p\omega_p)^2)} \quad (4.34)$$

assuming we may neglect damping factors; for b odd the $\pm \rightarrow \mp$. As the nonresonant limit is approached we may expand each denominator factor in Eq.(4.34) as a power series in g , for example the first factor is expanded:

$$\frac{1}{(E_{i,s_1}^2 - (\hbar\eta_1\omega_1)^2)} = \frac{1}{(E_{i,s_1})^2} \sum_{m=0}^{\infty} \left(\frac{\hbar\eta_1\omega_1}{E_{i,s_1}} \right)^{2m}. \quad (4.35)$$

It is then seen that for b even

$$\begin{aligned} \frac{1}{\mathcal{D}_{fi+;b}^{\{\eta\}\{s\}}} &\propto g^0 + g^2 + g^4 + \dots, \\ \frac{1}{\mathcal{D}_{fi-;b}^{\{\eta\}\{s\}}} &\propto g^1 + g^3 + g^5 + \dots, \end{aligned} \quad (4.36)$$

and vice versa for b odd. In particular, because

$$\frac{1}{D_{fi}^{\{\eta\}\{s\}}} = \frac{1}{D_{fi}^{\{0\}\{s\}}} \left(1 + \sum_{n=1}^{N-1} \frac{\sum_{k=1}^n \eta_k \hbar\omega_k}{E_{i,s_n}} + O(g^2) \right), \quad (4.37)$$

for b even

$$\langle f | O_{\{\mathbf{k}\}+,b}^{\{\alpha,\eta\}} | i \rangle = \sum_{\{s\}} \frac{\sum_{\pi\{\alpha\}} N_{fi\pi\{\mathbf{k}\};b}^{\pi\{\alpha,\eta\}\{s\}}}{D_{fi}^{\{0\}\{s\}}} + O(g^2), \quad (4.38)$$

$$\langle f | O_{\{\mathbf{k}\}-,b}^{\{\alpha,\eta\}} | i \rangle = \sum_{\pi\{\alpha\},\{s\}} \frac{N_{fi\pi\{\mathbf{k}\};b}^{\pi\{\alpha,\eta\}\{s\}}}{D_{fi}^{\{0\}\{s\}}} \left(\sum_{n=1}^{N-1} \frac{\pi (\sum_{k=1}^n \eta_k \hbar\omega_k)}{E_{i,s_n}} \right) + O(g^3), \quad (4.39)$$

so that in the nonresonant limit $\langle f | O_{\{\mathbf{k}\}+,b}^{\{\alpha,\eta\}} | i \rangle$ tends quadratically to $\langle f | O_{\{\mathbf{k}\};b}^{\{\alpha,\eta\}} | i \rangle$, while $\langle f | O_{\{\mathbf{k}\}-,b}^{\{\alpha,\eta\}} | i \rangle$ tends linearly to zero. The converse holds if b is odd.

From Eqs.(3.57) and (4.39), the magnetic dipole contribution to coherent processes tends to zero linearly in g (c.f. Eq.(4.26)). Similarly, from Eqs.(4.29) and (4.38) the electric dipole and quadrupole terms tend to zero linearly for transitions between T-conjugate states in Kramers systems (c.f. Eq.(4.30)). If g is much less than the fine structure constant ($\simeq 1/137$), the magnetic dipole term

then dominates for these transitions (we have assumed that the ratio of the numerators may be approximated as the ratio of an electric and magnetic dipole matrix element; see also Eq.(4.45)). As compared to the selection rules in §4.3.2, these results allow for a more accurate estimation of the relative importance of the various multipole contributions in the nonresonant limit.

There have been several studies on the existence of Kleinman symmetry forbidden terms in the transition amplitude in situations where the nonresonant limit is not valid. For example, such terms have been measured by Crane and Bergman [36] and Lynch *et al.* [95] in crystals, and Wagnière [136] has given a discussion applicable to single molecules. Levine [89], in discussing second-harmonic generation and sum-frequency generation in crystals, has shown the deviation from Kleinman symmetry to be of order g^2 , which is in good agreement with the experimental data provided in that work. From Eqs.(4.26) and (4.38), our analysis also shows the convergence to Kleinman symmetry in coherent processes is quadratic rather than linear in g . This reproduces the result of Levine [89] (whose analysis involves what amounts to the same methods as used here) and shows that such a convergence exists for all other processes.

4.3.4 Examples

We illustrate the results of §§4.3.2 and 4.3.3 using the example of Rayleigh scattering. From Eq.(2.32), near the nonresonant limit the electronic parts of the transition amplitude take the form

$$\begin{aligned} O_{fi\{k\}}^{\{\alpha,\eta\}} \Big|_{\text{RS}} &= \sum_s \frac{\langle f | \xi_{\alpha_2}^{+,k_2} | s \rangle \langle s | \xi_{\alpha_1}^{-,k_1} | i \rangle}{E_{i,s}} (1 - g + g^2 + \dots) \\ &\quad + \frac{\langle f | \xi_{\alpha_1}^{-,k_1} | s \rangle \langle s | \xi_{\alpha_2}^{+,k_2} | i \rangle}{E_{i,s}} (1 + g + g^2 + \dots), \end{aligned} \quad (4.40)$$

where $g = \hbar\omega/E_{i,s}$. In the nonresonant limit we set $g = 0$.

The rule given in Eq.(4.26) reduces to

$$\begin{aligned} \text{Av}_i O_{ii\{M1\}}^{\{\alpha,0\}} \Big|_{\text{RS}} &= \text{Av}_i \sum_s \left(\frac{\langle i | m_{\alpha_2} | s \rangle \langle s | \mu_{\alpha_1} | i \rangle}{E_{i,s}} + \frac{\langle i | \mu_{\alpha_1} | s \rangle \langle s | m_{\alpha_2} | i \rangle}{E_{i,s}} \right. \\ &\quad \left. + \frac{\langle i | \mu_{\alpha_2} | s \rangle \langle s | m_{\alpha_1} | i \rangle}{E_{i,s}} + \frac{\langle i | m_{\alpha_1} | s \rangle \langle s | \mu_{\alpha_2} | i \rangle}{E_{i,s}} \right) \\ &= - \text{Av}_i \sum_s \left(\frac{\langle i | \mu_{\alpha_1} | s \rangle \langle s | m_{\alpha_2} | i \rangle}{E_{i,s}} + \frac{\langle i | m_{\alpha_2} | s \rangle \langle s | \mu_{\alpha_1} | i \rangle}{E_{i,s}} \right. \\ &\quad \left. + \frac{\langle i | m_{\alpha_1} | s \rangle \langle s | \mu_{\alpha_2} | i \rangle}{E_{i,s}} + \frac{\langle i | \mu_{\alpha_2} | s \rangle \langle s | m_{\alpha_1} | i \rangle}{E_{i,s}} \right) \\ &= - \text{Av}_i O_{ii\{M1\}}^{\{\alpha,0\}} \Big|_{\text{RS}}, \end{aligned} \quad (4.41)$$

when considering the magnetic dipole contribution to coherent Rayleigh scattering.

For incoherent Rayleigh scattering between T-conjugate states in Kramers systems Eq.(4.30) takes the form

$$\begin{aligned}
 O_{ii\{0\}}^{\{\alpha,0\}} \Big|_{\text{RS}} &= \sum_s \frac{\langle \bar{i} | \mu_{\alpha 2} | s \rangle \langle s | \mu_{\alpha 1} | i \rangle}{E_{i,s}} + \frac{\langle \bar{i} | \mu_{\alpha 1} | s \rangle \langle s | \mu_{\alpha 2} | i \rangle}{E_{i,s}} \\
 &= \sum_s -\frac{\langle \bar{i} | \mu_{\alpha 1} | s \rangle \langle s | \mu_{\alpha 2} | i \rangle}{E_{i,s}} - \frac{\langle \bar{i} | \mu_{\alpha 2} | s \rangle \langle s | \mu_{\alpha 1} | i \rangle}{E_{i,s}} \\
 &= -O_{ii\{0\}}^{\{\alpha,0\}} \Big|_{\text{RS}}, \tag{4.42}
 \end{aligned}$$

$$\begin{aligned}
 O_{ii\{M1\}}^{\{\alpha,0\}} \Big|_{\text{RS}} &= \sum_s \left(\frac{\langle \bar{i} | m_{\alpha 2} | s \rangle \langle s | \mu_{\alpha 1} | i \rangle}{E_{i,s}} + \frac{\langle \bar{i} | \mu_{\alpha 1} | s \rangle \langle s | m_{\alpha 2} | i \rangle}{E_{i,s}} \right. \\
 &\quad \left. + \frac{\langle \bar{i} | \mu_{\alpha 2} | s \rangle \langle s | m_{\alpha 1} | i \rangle}{E_{i,s}} + \frac{\langle \bar{i} | m_{\alpha 1} | s \rangle \langle s | \mu_{\alpha 2} | i \rangle}{E_{i,s}} \right) \\
 &= + \sum_s \left(\frac{\langle \bar{i} | \mu_{\alpha 1} | s \rangle \langle s | m_{\alpha 2} | i \rangle}{E_{i,s}} + \frac{\langle \bar{i} | m_{\alpha 2} | s \rangle \langle s | \mu_{\alpha 1} | i \rangle}{E_{i,s}} \right. \\
 &\quad \left. + \frac{\langle \bar{i} | m_{\alpha 1} | s \rangle \langle s | \mu_{\alpha 2} | i \rangle}{E_{i,s}} + \frac{\langle \bar{i} | \mu_{\alpha 2} | s \rangle \langle s | m_{\alpha 1} | i \rangle}{E_{i,s}} \right) \\
 &= +O_{ii\{M1\}}^{\{\alpha,0\}} \Big|_{\text{RS}}, \tag{4.43}
 \end{aligned}$$

at the electric and magnetic dipole levels.

The lowest order correction to Eq.(4.42) is

$$O_{ii\{0\}}^{\{\alpha,0\}} \Big|_{\text{RS}} = \sum_s \left(-\frac{\langle \bar{i} | \mu_{\alpha 2} | s \rangle \langle s | \mu_{\alpha 1} | i \rangle}{E_{i,s}} + \frac{\langle \bar{i} | \mu_{\alpha 1} | s \rangle \langle s | \mu_{\alpha 2} | i \rangle}{E_{i,s}} \right) g. \tag{4.44}$$

Hence,

$$\frac{O_{ii\{0\}}^{\{\alpha,0\}} \Big|_{\text{RS}}}{O_{ii\{M1\}}^{\{\alpha,0\}} \Big|_{\text{RS}}} \simeq 137g, \tag{4.45}$$

assuming the ratio of the parts in brackets may be approximated as the ratio of an electric and magnetic dipole matrix element ($\simeq 137$). This illustrates the discussion following Eq.(4.39).

Finally, the parts of the electric dipole contribution to coherent Rayleigh scattering that are linear in g are

$$\text{Av}_i O_{ii\{0\}}^{\{\alpha,0\}} \Big|_{\text{RS}} = \text{Av}_i \sum_s \left(-\frac{\langle \bar{i} | \mu_{\alpha 2} | s \rangle \langle s | \mu_{\alpha 1} | i \rangle}{E_{i,s}} + \frac{\langle \bar{i} | \mu_{\alpha 1} | s \rangle \langle s | \mu_{\alpha 2} | i \rangle}{E_{i,s}} \right) g, \tag{4.46}$$

which is readily seen to be zero by HT symmetry. This illustrates that the deviation from Kleinman symmetry is quadratic in g , as discussed at the end of §4.3.3.

4.4 Coulomb gauge

In the nonresonant limit the time reversal selection rules found in the Coulomb gauge appear to differ from those found in the multipolar gauge (§4.4.1). To verify that identical results follow in either gauge, a careful comparison of the effective transition operators is required (§§4.4.2 and 4.4.3).

4.4.1 Apparent selection rules

When damping factors may be ignored, the transition amplitude in the Coulomb gauge may be obtained from the multipolar gauge amplitude by substituting into it the Coulomb gauge interaction Hamiltonian (§2.5). In analogy with Eq.(4.9), the final relation of Eq.(3.44) may be rewritten:

$$\left(\overline{\xi_{\alpha;\text{Coul}}^{\eta,k}}\right)^\dagger = -\xi_{\alpha;\text{Coul}}^{\eta,k}. \quad (4.47)$$

In the nonresonant limit the HT signature of the effective transition operator then appears to be $(-1)^N$, regardless of the multipole level (see Eq.(3.45)):

$$\left(\overline{O_{\{\mathbf{k}\};\text{Coul}}^{\{\alpha,\eta\}}}\right)^\dagger \stackrel{?}{=} (-1)^N O_{\{\mathbf{k}\};\text{Coul}}^{\{\alpha,\eta\}}. \quad (4.48)$$

The paradoxical situation therefore exists where the rules found in the Coulomb gauge seem to differ from the rules found in the multipolar gauge (§4.3.2). For example, Eq.(4.48) suggests that odd-order (N odd) coherent processes such as second-harmonic generation are suppressed in the Coulomb gauge, whereas there is no such restriction in the multipolar gauge (Eq.(4.26)).

Although the transition amplitudes found in the two gauges are equivalent (see Eq.(2.60)), the photon and electronic parts are not separately equal. In particular, if the mode k_1 involves absorption then $\gamma_{\{\alpha\}}^{\{n'_k n_k\}}$ and $\gamma_{\{\alpha\};\text{Coul}}^{\{n'_k n_k\}}$ contain

$$i\phi_1 c_{k_1} \langle n_{k_1} - 1 | a_{k_1} | n_{k_1} \rangle (e_{k_1})_{\alpha_1}, \quad \phi_1 \omega_{k_1}^{-1} c_{k_1} \langle n_{k_1} - 1 | a_{k_1} | n_{k_1} \rangle (e_{k_1})_{\alpha_1}, \quad (4.49)$$

respectively (the corresponding relation in classical electromagnetism is $\mathcal{E}(\omega_{k_1}) = i\omega_{k_1} \mathcal{A}(\omega_{k_1})$). Hence the ω dependence of $\gamma_{\{\alpha\}}^{\{n'_k n_k\}}$ is ω^N times that of $\gamma_{\{\alpha\};\text{Coul}}^{\{n'_k n_k\}}$:

$$\gamma_{\{\alpha\}}^{\{n'_k n_k\}} \propto \omega^N \gamma_{\{\alpha\};\text{Coul}}^{\{n'_k n_k\}}. \quad (4.50)$$

Verifying that identical selection rules are obtained in either gauge involves comparing the ω dependence of electronic parts of the transition amplitude, given Eq.(4.50). For clarity we first consider the verification in the electric dipole approximation before discussing the general case.

4.4.2 Electric dipole approximation

Following an identical procedure as in Eq.(4.36), the HT symmetrised parts of the effective transition operator may be expanded in a power series:

$$\begin{aligned} O_{\{0\}+}^{\{\alpha,\eta\}} &\propto \omega^0 + \omega^2 + \omega^4 + \dots, \\ O_{\{0\}-}^{\{\alpha,\eta\}} &\propto \omega^1 + \omega^3 + \omega^5 + \dots; \end{aligned} \quad (4.51)$$

because in the electric dipole approximation the numerator parts of the transition amplitude are independent of ω , we have rewritten the g dependence as a ω dependence. Similarly, from Eq.(4.47) we have for N even

$$\begin{aligned} O_{\{0\}+;\text{Coul}}^{\{\alpha,\eta\}} &\propto \omega^0 + \omega^2 + \omega^4 + \dots, \\ O_{\{0\}-;\text{Coul}}^{\{\alpha,\eta\}} &\propto \omega^1 + \omega^3 + \omega^5 + \dots, \end{aligned} \quad (4.52)$$

and vice versa for N odd. Because the ω dependence of $O_{fi\{0\}}^{\{\alpha,\eta\}}$ and $O_{fi\{0\};\text{Coul}}^{\{\alpha,\eta\}}$ are the same, gauge invariance (Eq.(2.60)) together with Eq.(4.50) requires the lowest N terms in the power series expansion of $O_{fi\{0\};\text{Coul}}^{\{\alpha,\eta\}}$ to be zero. Hence, the first nonzero term, namely that of order ω^N , must be considered when deriving selection rules in the Coulomb gauge. This shows the paradox cannot be resolved using time reversal arguments alone, in particular HT symmetry cannot be used to cancel all of these lowest N terms.

Equations (4.52) show that in the Coulomb gauge the ω^N term is in the time-even (HT symmetric) part of $O_{\{0\};\text{Coul}}^{\{\alpha,\eta\}}$. Hence Eq.(4.48) is incorrect, the HT signature is +1 for all N . Equations (4.26) and (4.30) thus agree between the gauges. Similarly, gauge invariance requires the ω^N term to be symmetric on all the Cartesian labels, and Eq.(4.52) shows that the deviation from this is quadratic, verifying the gauge invariance of the index symmetry predictions at the end of §4.3.3. Thus, upon a careful application of gauge invariance, we have shown that all of the selection rules in §4.3.2 are identical in both the multipolar and Coulomb gauges, resolving the paradox in the electric dipole approximation. We have further shown the rules are found most directly in the multipolar gauge.

4.4.3 General case

In order to show the selection rules are identical in the electric dipole approximation, we compared the ω dependence of the effective transition operator in the multipolar gauge with that in the Coulomb gauge (§4.4.2). Beyond the electric dipole approximation the effective operator depends on the photon wavevectors $\{\mathbf{k}\}$. To show the rules are the same in this case we now not only compare the ω dependence, but also the $\hat{\mathbf{k}}$ dependence; $\hat{\mathbf{k}}$ is a generic term which denotes a unit wavevector of an arbitrary participating photon. In particular, we expand the energy denominators of the effective operator in the multipolar gauge as a

power series in g (as in Eq.(4.36)), and consider the parts with a g^0 dependence and a fixed power of $\hat{\kappa}$. This expression is then compared with the parts of the effective operator in the Coulomb gauge with that ω and $\hat{\kappa}$ dependence.

To begin consider the contributions to the multipolar gauge expression that involve only $\Lambda_{\alpha}^{\eta, \mathbf{k}}$ -type interactions (i.e. have $b = 0$), which by Eq.(4.24) are in the time-even part. The corresponding term in the Coulomb gauge is of order g^N (compare Eq.(4.7) with Eq.(2.46)). Using a similar logic as in §4.4.2, this is also in the time-even part. Next consider a multipolar gauge contribution of the same type as just mentioned but with one $\Upsilon_{\alpha}^{\eta, \mathbf{k}}$ -type interaction replacing a $\Lambda_{\alpha}^{\eta, \mathbf{k}}$ -type interaction (i.e. $b = 1$ parts). By Eq.(4.24) this is in the time-odd part. The corresponding term in the Coulomb gauge is of order g^{N-1} (compare Eq.(4.8) with Eq.(2.46)) and is also in the time-odd part. Similarly, the multipolar gauge contribution formed on replacing b $\Lambda_{\alpha}^{\eta, \mathbf{k}}$ -type interactions with b $\Upsilon_{\alpha}^{\eta, \mathbf{k}}$ -type interactions is in the time-even part if $(-1)^b$ is $+1$ and is in the time-odd part if $(-1)^b$ is -1 (Eq.(4.24)). The corresponding term in the Coulomb gauge is of order g^{N-b} . This is also in the time-even part if b is even and in the time-odd part if b is odd.

We have thus verified that in the nonresonant limit the HT signatures of the effective transition operator in the multipolar and Coulomb gauges are equivalent at all multipole levels. The gauge invariance of time reversal selection rules follows directly from this.

4.4.4 Examples

We illustrate the arguments of §4.4.3 when applied to Rayleigh scattering. We define $\Lambda_{\alpha; n}^{\eta, \mathbf{k}}$ and $\Upsilon_{\alpha; n}^{\eta, \mathbf{k}}$ to be the parts of Eqs.(4.7) and (4.8) respectively that have a \mathbf{k}^n dependence. Similarly, from Eq.(2.46)) we define

$$\xi_{\alpha; \text{Coul}; n}^{\eta, \mathbf{k}} \equiv \sum_{\beta} -\frac{q_{\beta}}{m_{\beta}} (-i\eta \mathbf{k} \cdot \mathbf{r}_{\beta})^n (\mathbf{p}_{\beta})_{\alpha} + \frac{q_{\beta}^2}{2m_{\beta}c^2} (-i\eta \mathbf{k} \cdot \mathbf{r}_{\beta})^n (\mathbf{s}_{\beta} \times \mathbf{E}_{\text{C}}(\mathbf{r}_{\beta}))_{\alpha}. \quad (4.53)$$

In the nonresonant limit, the parts of the effective transition operator that have a $\hat{\kappa}^L$ dependence may then be separated into three terms:

$$\begin{aligned} O_{\{L\}}^{\{\alpha, \eta\}} \Big|_{\text{RS}} = & \sum_{n+m=L} \sum_s \left(\frac{\Lambda_{\alpha_2; m}^{+, \mathbf{k}_2} |s\rangle \langle s| \Lambda_{\alpha_1; n}^{-, \mathbf{k}_1}}{E_{i, s}} + \frac{\Lambda_{\alpha_1; n}^{-, \mathbf{k}_1} |s\rangle \langle s| \Lambda_{\alpha_2; m}^{+, \mathbf{k}_2}}{E_{i, s}} \right) \\ & + \sum_{n+m=L} \sum_s \left(\frac{\Upsilon_{\alpha_2; m}^{+, \mathbf{k}_2} |s\rangle \langle s| \Lambda_{\alpha_1; n}^{-, \mathbf{k}_1}}{E_{i, s}} + \frac{\Lambda_{\alpha_1; n}^{-, \mathbf{k}_1} |s\rangle \langle s| \Upsilon_{\alpha_2; m}^{+, \mathbf{k}_2}}{E_{i, s}} \right. \\ & \left. + \frac{\Lambda_{\alpha_2; m}^{+, \mathbf{k}_2} |s\rangle \langle s| \Upsilon_{\alpha_1; n}^{-, \mathbf{k}_1}}{E_{i, s}} + \frac{\Upsilon_{\alpha_1; n}^{-, \mathbf{k}_1} |s\rangle \langle s| \Lambda_{\alpha_2; m}^{+, \mathbf{k}_2}}{E_{i, s}} \right) \\ & + \sum_{n+m=L} \sum_s \left(\frac{\Upsilon_{\alpha_2; m}^{+, \mathbf{k}_2} |s\rangle \langle s| \Upsilon_{\alpha_1; n}^{-, \mathbf{k}_1}}{E_{i, s}} + \frac{\Upsilon_{\alpha_1; n}^{-, \mathbf{k}_1} |s\rangle \langle s| \Upsilon_{\alpha_2; m}^{+, \mathbf{k}_2}}{E_{i, s}} \right), \end{aligned}$$

which have HT signatures $+1, -1, +1$ respectively. As discussed in §4.4.3, the corresponding terms in the Coulomb gauge are:

$$\begin{aligned}
O_{\{L\};\text{Coul}}^{\{\alpha,\eta\}} \Big|_{\text{RS}} &= \sum_{n+m=L} \sum_s \left(\frac{\xi_{\alpha_2;\text{Coul};m}^{+,k_2} |s\rangle \langle s| \xi_{\alpha_1;\text{Coul};n}^{-,k_1}}{E_{i,s}} + \frac{\xi_{\alpha_1;\text{Coul};n}^{-,k_1} |s\rangle \langle s| \xi_{\alpha_2;\text{Coul};m}^{+,k_2}}{E_{i,s}} \right) \\
&+ \sum_{n+m=L} \sum_s \left(-\frac{\xi_{\alpha_2;\text{Coul};m}^{+,k_2} |s\rangle \langle s| \xi_{\alpha_1;\text{Coul};n}^{-,k_1}}{E_{i,s}} + \frac{\xi_{\alpha_1;\text{Coul};n}^{-,k_1} |s\rangle \langle s| \xi_{\alpha_2;\text{Coul};m}^{+,k_2}}{E_{i,s}} \right) g \\
&+ \sum_{n+m=L} \sum_s \left(\frac{\xi_{\alpha_2;\text{Coul};m}^{+,k_2} |s\rangle \langle s| \xi_{\alpha_1;\text{Coul};n}^{-,k_1}}{E_{i,s}} + \frac{\xi_{\alpha_1;\text{Coul};n}^{-,k_1} |s\rangle \langle s| \xi_{\alpha_2;\text{Coul};m}^{+,k_2}}{E_{i,s}} \right) g^2,
\end{aligned}$$

which also have HT signatures $+1, -1, +1$ respectively. That is, the HT signatures of the effective transition operator are the same in both gauges.

5. Nonlinear natural optical activity

Optical activity has traditionally been thought to require the interference of the contributing electric and magnetic dipole terms of the scattering intensity. This selection rule may be derived using time reversal symmetry. Recent experimental and theoretical work has however shown that if intermediate resonances are present, purely electric dipole contributions are possible. Here we modify standard time reversal selection rules to account for intermediate resonances, thereby reproducing and extending these recent results (§5.2.1). The magnitude of the purely electric dipole effect is compared with the magnitude of the traditional effect (§5.2.2). Selection rules associated with parity are briefly discussed (§5.2.5).

5.1 Introduction

Optical activity has been of scientific interest ever since its discovery over 150 years ago. For example, early workers such as Pasteur and Fresnel realised that optical rotation requires molecules which possess handedness - this idea has subsequently developed into the field of stereochemistry. In the mid-'70s technological improvements allowed for optical activity measurements in Rayleigh and Raman scattering, including vibrational optical activity [13], stimulating much discussion (Hecht and Barron [61] and references therein). Optical activity measurements have also been of interest in studying parity violations in atomic systems due to the weak interaction [127].

A classical description of optical rotation was given by Drude in 1893, which followed on from the ideas of Boltzmann. The corresponding quantum mechanical formulation was developed by Rosenfeld in 1928. That formulation is now standard and gives the optical rotation angle in terms of the interference between electric and magnetic dipole moments [13]. Incidentally, Nieves and Pal [107] show how this quantum description may be recast in terms of a classical theory by introducing a third electromagnetic constant (in addition to the dielectric and magnetic permeability constants).

In the early '80s the concept of optical activity was extended from linear to nonlinear optics. The first step was taken by Andrews and Thirunamachandran [10] who considered the difference in scattering intensity in hyper-Raman scattering when the input photons are left or right circularly polarised. The theory was subsequently developed for second-harmonic generation [79], sum and difference frequency generation and four wave mixing [135]. As in the linear case, these analyses found that multipole contributions beyond the electric dipole are required.

Although these theoretical predictions of nonlinear optical activity have been known for some time, the corresponding experiments have not been carried out until recently. The first examination was done by Petralli-Mallow *et al.* [112] on the intensity difference in second-harmonic generation from isotropic surfaces when the harmonic beam is linearly polarised and the input beam either has left or right circular polarisation. They found this difference to be on the order of the input intensity for near resonant conditions. This result is not explained by the theory developed by previous workers as the requirement of magnetic dipole terms results in a much smaller effect [10, 79, 135]. Petralli-Mallow *et al.* [112] postulated an electric dipole mechanism to account for their very large optical activity measurements. Their ideas were formalised in Byers *et al.* [27] where they showed the inclusion of damping factors allows for purely electric dipole contributions to optical activity. Because intermediate resonances were not considered by previous workers [10, 79, 135], this possibility had not been previously realised. Hecht and Barron [62] have subsequently shown that optical activity in Rayleigh and Raman scattering is also electric dipole allowed for near resonant conditions.

Shortly after the investigation of Petralli-Mallow *et al.* [112], Kauranen *et al.* [75] considered the same type of process but without intermediate resonances. They found the dominating mechanism for optical activity in that case requires magnetic dipole terms as described by earlier treatments [10, 79, 135]. The problem was further discussed by that group in Maki *et al.* [97] who noted that purely electric dipole contributions are indeed possible near resonance. Other related papers are Verbiest *et al.* [134] who consider anisotropic surfaces and Byers *et al.* [26] who consider the second-harmonic generation version of optical rotation; linear optical rotation is considered by Hecht and Barron [62].

Time reversal symmetry has been profitably employed in discussions of optical activity. For example, Hecht and Barron [61] have symmetrised the effective transition operator with respect to H and T in their examinations of various forms of optical activity in Rayleigh and Raman scattering. Also, Stedman [128, 130] has applied T symmetry to the electronic parts of the scattering intensity to derive practical selection rules for the intensity difference, ΔI , between a process and that process with its polarisation vectors complex conjugated (see Fig. 5.1):

$$\Delta I \equiv I^{\{n'_k n_k\}} - I^{\{n'_k^* n_k^*\}}. \quad (5.1)$$

The process under consideration may be linear or nonlinear, parametric or non-

parametric, coherent or incoherent (hence no ‘coh’ or ‘incoh’ label is included). The asterisk denotes the transformation to complex conjugate polarisations:

$$k^* \equiv (\mathbf{k}, \mathbf{e}_k^*), \quad (5.2)$$

so that left and right circular polarisations are interchanged and linear polarisations are unaffected (ΔI is therefore the parts of $I^{\{n'_k n_k\}}$ that are inequivalent under $\{\mathbf{e}_k\} \rightarrow \{\mathbf{e}_k^*\}$). It was shown that optical activity is present ($\Delta I \neq 0$) if there is an odd number of wavevectors from higher multipole couplings, or if a net time-odd interaction is considered (e.g. electric and magnetic dipole interference). This reproduced previous results that had been derived for certain processes [10, 79, 135]. Here we extend the analysis of Stedman [128, 130] to allow for intermediate resonances. We reproduce the basic results of Byers *et al.* [27] and Hecht and Barron [62] and give circular intensity difference expressions for all other processes.

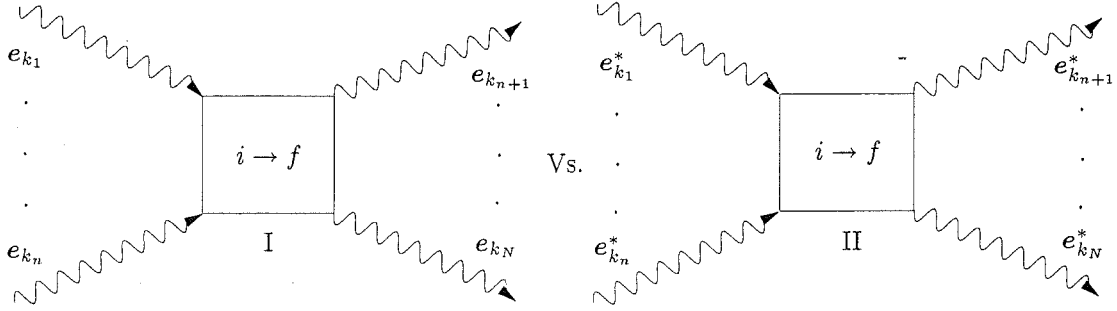


Fig. 5.1: In this chapter we consider the intensity difference between processes I and II. Process I differs from II only by the complex conjugation of all the polarisation vectors, i.e. II may be obtained from I by replacing each left circularly polarised photon with a right circularly polarised photon and visa versa (linear polarisations are unaffected).

5.2 Circular intensity difference

5.2.1 General expression

Because the photon number state $|n_{k^*}\rangle$ is defined such that it differs from $|n_k\rangle$ only by \mathbf{e}_k^* replacing \mathbf{e}_k , we have for example

$$\langle n_{k^*} - 1 | a_{k^*} | n_{k^*} \rangle = \langle n_k - 1 | a_k | n_k \rangle, \quad (5.3)$$

i.e. the photon matrix elements are the same. Hence,

$$\gamma_{\{\alpha\}}^{\{n'_{k^*} n_{k^*}\}} \left(\gamma_{\{\alpha'\}}^{\{n'_{k^*} n_{k^*}\}} \right)^* = \gamma_{\{\alpha\}}^{\{n'_k n_k\}} \left(\gamma_{\{\alpha\}}^{\{n'_k n_k\}} \right)^*. \quad (5.4)$$

This relation, together with application of T symmetry to the electronic parts of the transition amplitude (Eq.(3.12)), allows the scattering intensity (Eq.(2.13)) to be rewritten as follows

$$\begin{aligned} I^{\{n'_{k*}n_{k*}\}} &\propto \text{Av}_i \sum_f \sum_{\{\alpha\}, \{\alpha'\}} \gamma_{\{\alpha\}}^{\{n'_{k*}n_{k*}\}} \left(\gamma_{\{\alpha'\}}^{\{n'_{k*}n_{k*}\}} \right)^* O_{fi\{\mathbf{k}\}}^{\{\alpha, \eta\}} \left(O_{fi\{\mathbf{k}\}}^{\{\alpha', \eta\}} \right)^* \\ &= \text{Av}_i \sum_f \sum_{\{\alpha\}, \{\alpha'\}} \left(\gamma_{\{\alpha\}}^{\{n'_{k*}n_{k*}\}} \right)^* \gamma_{\{\alpha'\}}^{\{n'_{k*}n_{k*}\}} \left(O_{fi\{-\mathbf{k}\}}^{\{\alpha, \eta, -\Gamma\}} \right)^* O_{fi\{-\mathbf{k}\}}^{\{\alpha', \eta, -\Gamma\}}, \end{aligned} \quad (5.5)$$

where we assume in this chapter that the sum over final states includes for every f its T-conjugate \bar{f} . Upon interchanging the dummy labels $\{\alpha\}$ and $\{\alpha'\}$, a comparison of Eqs.(2.13) and (5.5) shows that $I^{\{n'_{k*}n_{k*}\}}$ differs from $I^{\{n'_kn_k\}}$ by the operations $\{\mathbf{k}\} \rightarrow \{-\mathbf{k}\}$ and $\{\Gamma\} \rightarrow \{-\Gamma\}$ on the electronic parts; an identical result follows if Eq.(2.12) is used place of Eq.(2.13). Equation (5.5) allows selection rules to be derived on the circular intensity difference defined by Eq.(5.1).

In giving the T symmetry relation of Eq.(3.12), Stedman [130] does not use the $\{\mathbf{k}\} \rightarrow \{-\mathbf{k}\}$ notation and instead has

$$O_{fi\{L\}}^{\{\alpha, \eta\}} = \tau_L \left(O_{\bar{f}i\{L\}}^{\{\alpha, \eta\}} \right)^*. \quad (5.6)$$

As discussed in §§4.4.3 and 4.4.4, the L subscript indicates that the transition amplitude is being considered at the multipole levels where there are L photon wavevectors present. In particular, the exponentials, $e^{-i\eta\mathbf{k} \cdot \mathbf{r}_\beta}$, in the interaction Hamiltonian ξ (Eqs.(2.22) and (2.24)) may be expanded as a power series: $\sum_n (-i\eta\mathbf{k} \cdot \mathbf{r}_\beta)^n / n!$. Fixing the total number, R , of such $-i\eta\mathbf{k} \cdot \mathbf{r}_\beta$ factors arising from the N participating photon modes and also the number of modes, b , that involve magnetic-type interactions (Eq.(2.24) and the last two lines of Eq.(2.22)) specifies L : $L = R + b$. The T signature, τ_L , is

$$\tau_L = (-1)^{R+b} = (-1)^L. \quad (5.7)$$

Because T is antilinear ($TiT^{-1} = -i$) the $(-1)^R$ appears from the complex conjugation of the R terms $i\mathbf{k}$ within $O_{fi\{L\}}^{\{\alpha, \eta\}}$ (c.f. the HT phase associated with i which is $+1$). Because the momentum and spin operators are time-odd ($T\mathbf{p}T^{-1} = -\mathbf{p}$, $T\mathbf{s}T^{-1} = -\mathbf{s}$) the $(-1)^b$ arises as the time reversal signature of the associated multipoles (since these operators are hermitian the T and HT signatures are identical). For example, the electric dipole, magnetic dipole and electric quadrupole contributions have $R = b = 0$, $R = 0, b = 1$ and $R = 1, b = 0$ respectively.

Stedman [130] therefore has instead of the $\{-\mathbf{k}\}$ in Eq.(5.5), a phase $\tau'_L = (-1)^{R'+b'}$, which is a combination of the phases arising from the electronic parts of the amplitude and its complex conjugate. If damping is ignored in Eqs.(5.1) and (5.5), the first time reversal rule of Stedman [130] is obtained:

$$\tau'_L = \pm 1 \quad \Rightarrow \quad I^{\{n'_{k*}n_{k*}\}} \Big|_L = \pm I^{\{n'_kn_k\}} \Big|_L, \quad (5.8)$$

the -1 indicating the presence of differential scattering and $+1$ indicating the absence.

Stedman [130] has applied this rule to several examples. In the electric dipole approximation $\tau_L' = 1$ and no intensity difference exists. For nonzero differential scattering the interference of an $R = b = 0$ level with $R = 0, b = 1$ or $R = 1, b = 0$ level is required. This reproduces the standard result for both the linear and nonlinear case.

Stedman [130] also considers situations where external fields are present. The phase τ_L' then contains an additional contribution of $+1$ for an external electric field and -1 for a magnetic field. As shown by Faraday, all materials become optically active in the latter case. Stedman [130] incorporates these fields by including the corresponding interaction Hamiltonian, ϱ , in the unperturbed electronic Hamiltonian and then expanding the resultant basis to first order in that interaction:

$$|s\rangle \rightarrow |s\rangle + \sum_{s'} \frac{|s'\rangle \langle s'|\varrho|s\rangle}{E_{s,s'}}. \quad (5.9)$$

The electronic parts of the transition amplitude are then also taken to first order in ϱ , giving the described phase. We have not done this here but such an extension may be readily included. We thus only consider the case where external influences are absent and for this reason have included ‘natural’ in the title of this chapter.

We now return to Eq.(5.5), where nonzero damping factors are included. Now Eq.(5.8) no longer holds because of the $\{-\Gamma\}$ and therefore new effects are predicted. In particular, because

$$O_{fi\{0\}}^{\{\alpha,\eta,-\Gamma\}} \neq O_{fi\{0\}}^{\{\alpha,\eta\}}, \quad (5.10)$$

the circular intensity difference ΔI is nonzero at the purely electric dipole level (without the need for an external magnetic field). In the cases of second-harmonic generation and Rayleigh and Raman scattering this reproduces the results of Byers *et al.* [27] and Hecht and Barron [62]. The above analysis of Stedman [130] may be used in discussing these and other processes in and beyond the electric dipole approximation, but with appropriate modifications to account for the $\{-\Gamma\}$ in Eq.(5.5). Examples are given in §§5.2.3 and 5.2.4.

Incidentally, electric dipole contributions to circular dichroism in aligned molecules have been studied for some time [11, 30, 37]. The state of an atom or molecule with total angular momentum J is said to be aligned if the populations of the M_J sublevels are nonuniform (this nonuniformity may be achieved by, for example, polarised pumping). The reason why this process is electric dipole allowed is therefore because a statistical average is not appropriate (because this is a one photon process it is of course not possible to have intermediate resonances).

5.2.2 Electric and magnetic dipole contributions

Byers *et al.* [27] have measured the intensity difference in second-harmonic generation to be on the order of the input intensity for near resonant conditions,

i.e.

$$\frac{\Delta I|_{\text{SHG}}}{\frac{1}{2} (I^{\{n'_k n_k\}}|_{\text{SHG}} + I^{\{n'_{k*} n_{k*}\}}|_{\text{SHG}})} \simeq 1. \quad (5.11)$$

Hecht and Barron [62] estimate such a ratio is possible in Rayleigh and Raman scattering optical activity. In discussing second-harmonic generation, Kauranen *et al.* [75] and Maki *et al.* [97] isolate the parts of the intensity difference that involve pure electric dipole terms and those that involve the traditional interference of electric and magnetic dipole terms. Those workers discuss the relative importance of these two lowest order contributions to the intensity difference (Byers *et al.* [27] and Hecht and Barron [62] do not consider magnetic dipole terms). They conclude that unless strong resonances are present, the magnetic dipole contributions are the most important.

Here we estimate the relative magnitudes of the electric and magnetic dipole contributions to the circular intensity difference for a general nonlinear optical process. Although all such information is already contained within Eqs.(5.1) and (5.5), we consider a simplified situation in order to present the results in a more transparent form. In particular, we suppose that for those excited electronic states that are not near resonance the associated damping factors may be neglected. We further suppose the near resonance occurs only in one temporal ordering, say photon 1 interacting, then photon 2, ..., then photon N , and the contributions to the amplitude from all other temporal orderings may be neglected relative to this term. In this situation and in the electric dipole approximation

$$\begin{aligned} O_{fi\{0\}}^{\{\alpha, \eta\}} \left(O_{fi\{0\}}^{(\alpha', \eta)} \right)^* - O_{fi\{0\}}^{\{\alpha, \eta, -\Gamma\}} \left(O_{fi\{0\}}^{(\alpha', \eta, -\Gamma)} \right)^* = \\ \sum_{\{s\}, \{s'\}} \sum_{e, e'} \left[\left(\frac{N_{fi\{0\}}^{\{\alpha, \eta\}\{s; e\}}}{\hat{D}_{fi}^{\{\eta\}\{s\}}(\Delta_e + i\Gamma_e)} \frac{\left(N_{fi\{0\}}^{\{\alpha', \eta\}\{s'; e'\}} \right)^*}{\hat{D}_{fi}^{\{\eta\}\{s'\}}(\Delta_{e'} - i\Gamma_{e'})} \right) \right. \\ \left. - \left(\frac{N_{fi\{0\}}^{\{\alpha, \eta\}\{s; e\}}}{\hat{D}_{fi}^{\{\eta\}\{s\}}(\Delta_e - i\Gamma_e)} \frac{\left(N_{fi\{0\}}^{\{\alpha', \eta\}\{s'; e'\}} \right)^*}{\hat{D}_{fi}^{\{\eta\}\{s'\}}(\Delta_{e'} + i\Gamma_{e'})} \right) \right], \end{aligned} \quad (5.12)$$

where the sum over e, e' runs over the excited states near resonance, Δ_e is the detuning:

$$\Delta_e = E_{i, e} - \hbar \sum_{p=1}^{N-1} \eta_p \omega_p, \quad (5.13)$$

and $\hat{D}_{fi}^{\{\eta\}\{s\}}$ is defined through the relation

$$\hat{D}_{fi}^{\{\eta\}\{s\}}(\Delta_e + i\Gamma_e) \equiv D_{fi}^{\{\eta\}\{s\}}, \quad (5.14)$$

i.e. $\hat{D}_{fi}^{\{\eta\}\{s\}}$ is $D_{fi}^{\{\eta\}\{s\}}$ less the denominator factor involving the near resonance (see Eq.(2.18)). Note, there are now fewer intermediate electronic state labels, s ,

to be summed over because sum over near resonance states has been separated; this is highlighted by the superscript in the numerator. Equation (5.12) may be rewritten as

$$2i \sum_{\{s\}, \{s'\}} \sum_{e, e'} \frac{N_{fi\{0\}}^{\{\alpha, \eta\}\{s; e\}}}{\hat{D}_{fi}^{\{\eta\}\{s\}}} \frac{\left(N_{fi\{0\}}^{\{\alpha', \eta\}\{s'; e'\}}\right)^*}{\hat{D}_{fi}^{\{\eta\}\{s'\}}} \left(\frac{\Delta_e \Gamma_{e'} - \Delta_{e'} \Gamma_e}{(\Delta_e^2 + \Gamma_e^2)(\Delta_{e'}^2 + \Gamma_{e'}^2)} \right). \quad (5.15)$$

In the limit of strong resonance, where $\Delta_e \simeq \Gamma_e$, ΔI is therefore of the same order as the input intensities. This is in agreement with the experimental results of Byers *et al.* [27] (Eq.(5.11)) and the discussion of Hecht and Barron [62] when attention is restricted to second-harmonic generation and Rayleigh and Raman scattering respectively.

When a magnetic dipole interaction replaces an electric dipole interaction there is a phase difference of +1 rather than -1 inside the square brackets in Eq.(5.12) (see §5.2.1). The resultant expression reduces to

$$2 \sum_{\{s\}, \{s'\}} \sum_{e, e'} \left(\frac{N_{fi\{0\}}^{\{\alpha, \eta\}\{s; e\}}}{\hat{D}_{fi}^{\{\eta\}\{s\}}} \frac{\left(N_{fi\{M1\}}^{\{\alpha', \eta\}\{s'; e'\}}\right)^*}{\hat{D}_{fi}^{\{\eta\}\{s'\}}} + \frac{N_{fi\{M1\}}^{\{\alpha, \eta\}\{s; e\}}}{\hat{D}_{fi}^{\{\eta\}\{s\}}} \frac{\left(N_{fi\{0\}}^{\{\alpha', \eta\}\{s'; e'\}}\right)^*}{\hat{D}_{fi}^{\{\eta\}\{s'\}}} \right) \times \left(\frac{\Delta_e \Delta_{e'} + \Gamma_e \Gamma_{e'}}{(\Delta_e^2 + \Gamma_e^2)(\Delta_{e'}^2 + \Gamma_{e'}^2)} \right). \quad (5.16)$$

The relative magnitudes of the electric and magnetic dipole contributions may be approximated from Eqs.(5.15) and (5.16):

$$\frac{\Delta I|_{E1}}{\Delta I|_{M1}} \simeq 137 \frac{\Delta_e \Gamma_{e'} - \Delta_{e'} \Gamma_e}{\Delta_e \Delta_{e'} + \Gamma_e \Gamma_{e'}}, \quad (5.17)$$

where we assume the ratio of the numerators may be approximated as the ratio of an electric and magnetic dipole matrix element ($\simeq 137$). In the limit of very weak resonance, the relative contribution of the electric dipole parts tends to zero (reproducing Eq.(5.8)). As resonance is approached the electric dipole contribution then begins to dominate. Because of the multiplicative factor 137, this domination does not require strong resonance, contrary to the claims of Kauranen *et al.* [75] and Maki *et al.* [97].

5.2.3 Examples

The intensity difference, $\Delta I|_{RS}$, for an incoherent Rayleigh scattering process from polarisation e_1 to polarisation e_2 is given by Eqs.(5.1) and (5.5) and is

proportional to

$$\begin{aligned} & \sum_f A_v \left| \sum_i \frac{\langle f | \mathbf{e}_2^* \cdot \boldsymbol{\mu} | s \rangle \langle s | \mathbf{e}_1 \cdot \boldsymbol{\mu} | i \rangle}{E_{i,s} + \hbar\omega + i\Gamma_s} + \frac{\langle f | \mathbf{e}_1 \cdot \boldsymbol{\mu} | s \rangle \langle s | \mathbf{e}_2^* \cdot \boldsymbol{\mu} | i \rangle}{E_{i,s} - \hbar\omega + i\Gamma_s} \right|^2 \\ & - \sum_f A_v \left| \sum_i \frac{\langle f | \mathbf{e}_2^* \cdot \boldsymbol{\mu} | s \rangle \langle s | \mathbf{e}_1 \cdot \boldsymbol{\mu} | i \rangle}{E_{i,s} + \hbar\omega - i\Gamma_s} + \frac{\langle f | \mathbf{e}_1 \cdot \boldsymbol{\mu} | s \rangle \langle s | \mathbf{e}_2^* \cdot \boldsymbol{\mu} | i \rangle}{E_{i,s} - \hbar\omega - i\Gamma_s} \right|^2, \end{aligned} \quad (5.18)$$

in the electric dipole approximation. For compactness we have not separated the polarisation vectors from the electronic parts of the amplitude (the proportionality constant is therefore the product of the two photon field intensities). Under the simplifying assumptions stated in §5.2.2, this reduces to

$$\Delta I|_{\text{RS;E1}} \propto 2 \sum_f A_v \sum_{e,e'} \text{Im} \{ R_e R_{e'}^* \} \left(\frac{\Delta_{e'} \Gamma_e - \Delta_e \Gamma_{e'}}{(\Delta_e^2 + \Gamma_e^2)(\Delta_{e'}^2 + \Gamma_{e'}^2)} \right) \quad (5.19)$$

(see Eq.(5.15)), where

$$R_e = \langle f | \mathbf{e}_2^* \cdot \boldsymbol{\mu} | e \rangle \langle e | \mathbf{e}_1 \cdot \boldsymbol{\mu} | i \rangle; \quad (5.20)$$

in this example the detuning is $\Delta_e = E_{i,e} + \hbar\omega$. At the magnetic dipole level an electric dipole interaction is replaced by a magnetic dipole interaction. Because of the time-odd nature of this interaction, the magnetic dipole contribution is of a similar form as Eq.(5.19) except real instead of imaginary parts are taken and a differing fraction is obtained (see Eq.(5.16)):

$$\Delta I|_{\text{RS;M1}} \propto 2 \sum_f A_v \sum_{e,e'} \text{Re} \{ R'_e R_{e'}^* + R_e R_{e'}'^* \} \left(\frac{\Delta_e \Delta_{e'} + \Gamma_e \Gamma_{e'}}{(\Delta_e^2 + \Gamma_e^2)(\Delta_{e'}^2 + \Gamma_{e'}^2)} \right), \quad (5.21)$$

where

$$R'_e = \langle f | \mathbf{e}_2^* \cdot \mathbf{m} | e \rangle \langle e | \mathbf{e}_1 \cdot \boldsymbol{\mu} | i \rangle + \langle f | \mathbf{e}_2^* \cdot \boldsymbol{\mu} | e \rangle \langle e | \mathbf{e}_1 \cdot \mathbf{m} | i \rangle \quad (5.22)$$

(see Eq.(4.18)).

In the case of second-harmonic generation the intensity difference, $\Delta I|_{\text{SHG}}$, is proportional to

$$\begin{aligned} & \left| A_v \sum_{s_1, s_2} \frac{\langle i | \mathbf{e}_2^* \cdot \boldsymbol{\mu} | s_2 \rangle \langle s_2 | \mathbf{e}_1 \cdot \boldsymbol{\mu} | s_1 \rangle \langle s_1 | \mathbf{e}_1 \cdot \boldsymbol{\mu} | i \rangle}{(E_{i,s_1} + \hbar\omega + i\Gamma_{s_1})(E_{i,s_2} + 2\hbar\omega + i\Gamma_{s_2})} + t' + t'' \right|^2 \\ & - \left| A_v \sum_{s_1, s_2} \frac{\langle i | \mathbf{e}_2^* \cdot \boldsymbol{\mu} | s_2 \rangle \langle s_2 | \mathbf{e}_1 \cdot \boldsymbol{\mu} | s_1 \rangle \langle s_1 | \mathbf{e}_1 \cdot \boldsymbol{\mu} | i \rangle}{(E_{i,s_1} + \hbar\omega - i\Gamma_{s_1})(E_{i,s_2} + 2\hbar\omega - i\Gamma_{s_2})} + t' + t'' \right|^2, \end{aligned} \quad (5.23)$$

where t' and t'' denote the two other temporal orderings not explicitly shown (see Eq.(6.14)). In this example we take the detuning to be $\Delta_e = E_{i,e} + 2\hbar\omega$, which

does not occur in t' and t'' so that those terms may be neglected. The intensity difference may then be reduced into the simplified form

$$\Delta I|_{\text{SHG;E1}} \propto 2 \sum_{e,e'} \text{Im} \{S_e S_{e'}^*\} \left(\frac{\Delta_{e'} \Gamma_e - \Delta_e \Gamma_{e'}}{(\Delta_e^2 + \Gamma_e^2)(\Delta_{e'}^2 + \Gamma_{e'}^2)} \right), \quad (5.24)$$

where

$$S_e = A_V \sum_i \frac{\langle i | \mathbf{e}_2^* \cdot \boldsymbol{\mu} | e \rangle \langle e | \mathbf{e}_1 \cdot \boldsymbol{\mu} | s_1 \rangle \langle s_1 | \mathbf{e}_1 \cdot \boldsymbol{\mu} | i \rangle}{(E_{i,s_1} + \hbar\omega)}, \quad (5.25)$$

(see Eq.(5.15)). The magnetic dipole parts of the intensity difference may be found in a similar manner as in Eq.(5.21) and are

$$\Delta I|_{\text{SHG;M1}} \propto 2 \sum_{e,e'} \text{Re} \{S'_e S_{e'}^* + S_e S_{e'}'^*\} \left(\frac{\Delta_e \Delta_{e'} + \Gamma_e \Gamma_{e'}}{(\Delta_e^2 + \Gamma_e^2)(\Delta_{e'}^2 + \Gamma_{e'}^2)} \right), \quad (5.26)$$

where

$$S'_e = A_V \sum_i \left(\frac{\langle i | \mathbf{e}_2^* \cdot \mathbf{m} | e \rangle \langle e | \mathbf{e}_1 \cdot \boldsymbol{\mu} | s_1 \rangle \langle s_1 | \mathbf{e}_1 \cdot \boldsymbol{\mu} | i \rangle}{(E_{i,s_1} + \hbar\omega)} + \frac{\langle i | \mathbf{e}_2^* \cdot \boldsymbol{\mu} | e \rangle \langle e | \mathbf{e}_1 \cdot \mathbf{m} | s_1 \rangle \langle s_1 | \mathbf{e}_1 \cdot \boldsymbol{\mu} | i \rangle}{(E_{i,s_1} + \hbar\omega)} + \frac{\langle i | \mathbf{e}_2^* \cdot \boldsymbol{\mu} | e \rangle \langle e | \mathbf{e}_1 \cdot \boldsymbol{\mu} | s_1 \rangle \langle s_1 | \mathbf{e}_1 \cdot \mathbf{m} | i \rangle}{(E_{i,s_1} + \hbar\omega)} \right) \quad (5.27)$$

5.2.4 Two photon absorption

Circular intensity difference in two photon absorption was first observed by Gunde and Richardson [54] in 1995. Their experiment involved photons of identical energy, both having either left or right circular polarisation. The material system consisted of Gd^{3+} in trigonal $\text{Na}_3[\text{Gd}(\text{C}_4\text{H}_4\text{O}_5)_3] \cdot 2\text{NaClO}_4 \cdot 6\text{H}_2\text{O}$. Because no intermediate resonances were present, Gunde and Richardson [54] were able to explain their results in terms of the traditional electric and magnetic dipole interference. Their experimental results were further analysed in Gunde *et al.* [53]. The model developed there (again using electric and magnetic dipole interference) allowed for numerical estimates of the circular intensity difference and a good agreement with experiment was reached.

Resonant two photon absorption in $\text{Tb}^{3+}:\text{LiYF}_4$ has been investigated by Huang *et al.* [64]. Their experiment involved two linearly polarised photons of differing energies, only one of which is near resonance with an excited level. By combining the methods of Huang *et al.* [64] with Gunde and Richardson [54] it ought therefore to be possible to measure the resonant two photon absorption circular intensity difference in rare earths.

The basic theoretical description involves a simple modification of Eq.(5.19). In particular, suppose photons of energy $\hbar\omega_1$ and $\hbar\omega_2$ are absorbed and the near

resonance is $\Delta_e = E_{i,e} + \hbar\omega_1$. The intensity difference in the electric dipole approximation is then proportional to

$$\Delta I|_{\text{TPA;E1}} \propto 2 \sum_f A_i^V \sum_{e,e'} \text{Im} \{A_e A_{e'}^*\} \left(\frac{\Delta_{e'} \Gamma_e - \Delta_e \Gamma_{e'}}{(\Delta_e^2 + \Gamma_e^2)(\Delta_{e'}^2 + \Gamma_{e'}^2)} \right), \quad (5.28)$$

where

$$A_e = \langle f | \mathbf{e}_2 \cdot \boldsymbol{\mu} | e \rangle \langle e | \mathbf{e}_1 \cdot \boldsymbol{\mu} | i \rangle. \quad (5.29)$$

The magnetic dipole contribution is given by a similar modification of Eq.(5.21). Note, because the intermediate states in the system considered by Gunde and Richardson [54] do not have energies between the initial and final energies, that system is not amenable to resonant two photon effects and the experimental setup of Huang *et al.* [64] would be a better starting point for testing Eq.(5.28).

5.2.5 Parity considerations

In addition to the time reversal selection rule of Eq.(5.8), Stedman [130] also gives a similar rule based on parity considerations. We briefly discuss the modifications to that rule which result when damping factors are included. We do not consider a general nonlinear optical process but instead forward Rayleigh scattering at the electric and magnetic dipole levels. It is expected that the following is readily generalisable to the nonlinear case, but at this stage is a only first step towards a complete analysis.

We adopt an over-tilde notation for parity conjugation:

$$P|s\rangle = |\tilde{s}\rangle \quad POP^{-1} = \tilde{O} \quad \langle f | O | i \rangle = \langle \tilde{f} | \tilde{O} | \tilde{i} \rangle, \quad (5.30)$$

where P is the parity operator. Because the position operator is parity-odd ($\tilde{\mathbf{r}} = -\mathbf{r}$), the transition amplitude

$$A_i^V O_{ii\{0\}}^{\{\alpha,0\}}|_{\text{RS}} = A_i^V \sum_{s_1} \frac{\langle i | \mu_{\alpha_2} | s_1 \rangle \langle s_1 | \mu_{\alpha_1} | i \rangle}{E_{i,s_1} + \hbar\omega + i\Gamma_{s_1}} + \frac{\langle i | \mu_{\alpha_1} | s_1 \rangle \langle s_1 | \mu_{\alpha_2} | i \rangle}{E_{i,s_1} - \hbar\omega + i\Gamma_{s_1}}, \quad (5.31)$$

transforms to

$$A_i^V O_{ii\{0\}}^{\{\alpha,0\}}|_{\text{RS}} = A_i^V \sum_{s_1} \frac{\langle \tilde{i} | \mu_{\alpha_2} | s_1 \rangle \langle s_1 | \mu_{\alpha_1} | \tilde{i} \rangle}{E_{\tilde{i},s_1} + \hbar\omega + i\Gamma_{s_1}} + \frac{\langle \tilde{i} | \mu_{\alpha_1} | s_1 \rangle \langle s_1 | \mu_{\alpha_2} | \tilde{i} \rangle}{E_{\tilde{i},s_1} - \hbar\omega + i\Gamma_{s_1}}, \quad (5.32)$$

where we have assumed the damping factors for parity conjugate states are equal ($\Gamma_s = \Gamma_{\tilde{s}}$) and that P commutes with the unperturbed electronic Hamiltonian so that the energies of parity conjugate states are also equal ($E_s = E_{\tilde{s}}$). A similar relation as in Eq.(5.32) holds at the magnetic dipole level but with an overall parity phase of -1 (since the angular momentum operator is parity-even).

In the case of fluid media, the average over states allows the over-tildes in Eq.(5.32) to be dropped for systems consisting of achiral molecules. The interference of Eq.(5.32) with the magnetic dipole contribution therefore vanishes for such systems. This parity selection rule reproduces the standard result and Stedman [130] shows that it extends to nonlinear optical process also. However, at the purely electric dipole level, which involves the interference of Eq.(5.32) with its complex conjugate, no such selection rule exists as the overall parity phase is +1. That is, chiral molecules are *not* required for a nonzero circular intensity difference if intermediate resonances are present. In a fluid (where a rotational average is required) the electronic and photon parts of the amplitude are contracted with $\delta_{\alpha_1\alpha_2}$ [9], so that, for example, an intensity difference exists between the two scattering processes $\mathbf{e}_{\mathbf{k},+} \rightarrow \mathbf{e}_{\mathbf{k},1}$ and $\mathbf{e}_{\mathbf{k},-} \rightarrow \mathbf{e}_{\mathbf{k},1}$ regardless of whether the molecules are chiral or achiral.

Note however, because of other spatial symmetries chirality may be required. For example, in their discussions of second-harmonic generation off isotropic surfaces Byers *et al.* [27] note that chiral molecules maximise the intensity difference effect. This condition is imposed by the two dimensional rotational average. Similarly, Hecht and Barron [62] show such restrictions also exist in incoherent Rayleigh and Raman scattering off isotropic surfaces. For anisotropic surfaces Verbiest *et al.* [134] note that chiral molecules are not necessary.

The above discussion is readily adapted for two photon absorption. In that case an identical result follows, namely that chiral molecules are not required for the purely electric dipole contribution to the circular intensity difference. Thus, for the experiment proposed in §5.2.4, the chiral system of Gunde and Richardson [54] is not necessary and the achiral system of Huang *et al.* [64] suffices. (Note, we have not considered the restrictions the relevant point group places on this process.)

6. Phenomenological damping of transition amplitudes

In Chap. 3 we derived three reversality theorems which express the H, T and HT symmetries of the transition amplitude (Eqs.(3.25) to (3.27)). Implicit in those derivations is the assumption that the phenomenological damping factors introduced into the energy denominator parts of the amplitude are all of the same sign (see Eq.(2.18)). In this chapter we justify this assumption. To do this we first prove that the damping factors must be incorporated in such a manner as to preserve the reversal theorem (§6.2). This, in combination with certain non-phenomenological discussions of damping [8, 34], is used to obtain the result (§§6.3.1 and 6.3.2).

The prescription we have adopted for the signs of the damping factors is inequivalent to the most commonly employed prescription. We show that this later prescription is incompatible with time reversal symmetry, and is therefore incorrect (§6.3.3). We propose an experimental test that will distinguish between the two prescriptions (§6.4).

6.1 Introduction

The theoretical formulation of nonlinear optical processes commonly entails representing the material response in terms of parameters characterising both its ground and various higher energy states. When one or other of the excited states differs from the initial state by any amount closely similar to the energy of one or more participating photons, resonance enhancement is observed to occur. In such cases it is necessary to include damping in the description to properly account for the finite optical amplification, or the detailed dispersion behaviour.

Apart from a few simple cases there are considerable difficulties associated with the treatment of optical damping in a non-phenomenological manner. In an ensemble situation, the various damping mechanisms, such as radiative, collisional or intramolecular vibrational redistribution damping, will often contribute simultaneously. In principle, the formalism of quantum field theory in statistical

physics will give the correct form of the transition amplitudes in such complex situations [126, 129], including the sign of the damping factors [8]. However, detailed calculation can be a formidable task [99] and commonly only a phenomenological treatment is tractable. One pragmatic alternative is to dispense with such damping and to apply the ensuing results only in frequency regions well away from resonance (e.g. Ref. [35]). Such an approach has the attraction of retaining a rigour which confers what in other quantum mechanical areas would be termed *ab initio* status. This approach is however limited, being not well suited to the analysis of dispersion effects.

Very close to resonance, or when very intense electromagnetic fields are present, standard perturbation theory is inappropriate and a two-level model (or a multi-level extension thereof) is invariably employed to describe for example Rabi flopping [4, 25]. Here we shall examine the case of weak resonances with moderate fields. In this situation, losses which usually characterise bulk or ensemble response may enter a formulation based on independent molecules so as to endow excited levels with a finite linewidth (see for example Refs. [70, 71]). This leads to the association of damping factors with the excited state wavefunctions, entering into the energy denominators of transition amplitudes as imaginary addenda [23]. The magnitude of each imaginary addendum carries the physically significant connotation of the lifetime of an excited state, and leads to Lorentzian lineshapes of appropriate and experimentally determinable width. We accept the pragmatic value of this damping concept.

Two prescriptions have been used in the literature for setting the signs of these imaginary terms. The most common prescription is to assign signs by time-ordering considerations. For example, in second harmonic generation, signs are chosen oppositely for interactions preceding and following the emission of the harmonic photon. This approach has been founded on such principles as causality [23] or a semiclassical formalism featuring the optical susceptibility [19, 41, 87, 121]. We show that nevertheless this prescription is inconsistent with time reversal symmetry. As discussed below, we adopt a fixed sign prescription where all these signs are identical [8].

6.2 Reversal theorem

We prove that damping factors, phenomenological or otherwise, must enter into the amplitude so as to preserve HT symmetry (§6.2.2). However, H and T symmetries need not separately hold when damping is included (§6.2.3).

6.2.1 Previous result

In this thesis we have considered the transition amplitude

$$\langle \{n'_k\} | \langle \{f\} | U(t, t_0) | \{i\} \rangle | \{n_k\} \rangle, \quad (6.1)$$

and the associated scattering intensity

$$I^{\{n'_k n_k\}} = \sum_{\{f\}} \frac{d}{dt} |\langle \{n'_k\} | \langle \{f\} | U(t, t_0) | \{i\} \rangle | \{n_k\} \rangle|^2. \quad (6.2)$$

The $\{n_k\}, \{n'_k\}$ refer to the initial and final states of the photon field and the $\{i\}, \{f\}$ refer to the initial and final states of the M particles making up material subsystem (Eq.(2.3)); $U(t, t_0)$ is the evolution operator. By assuming the particles are independent and identical Eq.(6.2) may be rewritten in terms of one-particle transition amplitudes (Eqs.(2.7) to (2.9)). The lowest order contribution to these amplitudes is found from a perturbative expansion of Eq.(6.1) (namely Eqs.(2.14) and (2.16) when the Γ 's in Eq.(2.18) are set equal to zero; see also §2.5.2). The resulting expression is singular as intermediate resonances are approached and therefore is inadequate for describing such cases.

As discussed in §6.1, the standard practice for accounting for intermediate resonances is to include in the energy denominator parts of the transition amplitude the phenomenological damping factors Γ . We also follow this strategy (see Eq.(2.18)). However, the signs we associate with those damping factors are different to certain commonly employed prescriptions. In particular, we fix the signs under the restriction that the reversal theorem holds (§6.3.1), whereas in other prescriptions the resulting amplitude violates this theorem (§6.3.3). In §6.2.2 we justify our assumption that damping factors must be included in such a manner as to preserve time reversal symmetry.

6.2.2 Generalised reversal theorem

For the system described in §2.5.1 (governed by $H_{\text{multipolar}}$), radiative damping is the only possible damping mechanism. For example, collisional damping requires interacting particles and vibrational redistribution damping requires the consideration of their vibrational modes. The phenomenological factors $i\Gamma_s$ in Eq.(2.18) model the combination of all such damping mechanisms. As mentioned, we will prove that the inclusion of these imaginary addenda cannot result in the violation time reversal symmetry. We thus require a reversal theorem applicable to interacting particles with all possible degrees of freedom accounted for.

When degrees of freedom other than electronic energy levels are considered $\{i\}, \{f\}$ cannot be used to describe the initial and final states of the material subsystem. To keep the following discussion as general as possible we shall not attempt to specify those states but rather denote them by the arbitrary kets $|\Psi\rangle, |\Phi\rangle$ respectively; we suppose the same photon states may still be employed. We include all the relevant interactions of the light-matter system in the Hamiltonian \mathcal{H} . Since the system is closed, \mathcal{H} is time-independent and the evolution operator in the Schrödinger picture has the formal solution [94]

$$U(t, 0) = e^{-i\mathcal{H}t/\hbar} \quad (6.3)$$

(a similar formal result holds for the system considered in §2.3.1). The transition amplitude now takes the form

$$\langle \{n'_k\} | \langle \Phi | e^{-i\mathcal{H}t/\hbar} | \Psi \rangle | \{n_k\} \rangle \quad (6.4)$$

(c.f. Eq.(6.1)). Because of their formal nature, Eqs.(6.3) and (6.4) are not useful in deriving detailed expressions. However, they are useful in deriving general results which relate the amplitudes of time-reversed processes.

We suppose only electrodynamical interactions are present so that \mathcal{H} is time-even. The evolution operator therefore has an exact HT signature of +1:

$$\left(e^{-i\mathcal{H}t/\hbar} \right)^\dagger = e^{-i\mathcal{H}t/\hbar}. \quad (6.5)$$

Hence, the application of time reversal symmetry to Eq.(6.4) gives

$$\langle \{n'_k\} | \langle \Phi | e^{-i\mathcal{H}t/\hbar} | \Psi \rangle | \{n_k\} \rangle \stackrel{\text{HT}}{=} \langle \{n_{\bar{k}}\} | \langle \bar{\Psi} | e^{-i\mathcal{H}t/\hbar} | \bar{\Phi} \rangle | \{n'_{\bar{k}}\} \rangle \quad (6.6)$$

(for simplicity we have suppressed the phase ϕ_2 , see Eq.(3.21)). Equation (6.6) requires the amplitudes for the transitions $|\Psi\rangle|\{n_k\}\rangle \rightarrow |\Phi\rangle|\{n'_k\}\rangle$ and $|\bar{\Phi}\rangle|\{n'_{\bar{k}}\}\rangle \rightarrow |\bar{\Psi}\rangle|\{n_{\bar{k}}\}\rangle$ to be equal. The states $\{n'_k\}, \{n_{\bar{k}}\}$ have been discussed in §3.1.2 and the form of the time reversal operator requires $\bar{\Psi}, \bar{\Phi}$ to be the motion reversed states with respect to Ψ, Φ (§2.1). Equation (6.6) thus proves that time reversal symmetry must hold for an arbitrary material subsystem interacting with a radiation field, and this may be considered as a generalised reversal theorem (as compared to Eq.(3.27)).

In situations where the particles interact weakly and the non-electronic degrees of freedom are of secondary importance, i.e. in situations where the treatment in §2.3 is appropriate, we have

$$\langle \{n'_k\} | \langle \Phi | e^{-i\mathcal{H}t/\hbar} | \Psi \rangle | \{n_k\} \rangle \simeq V_{\{f\}\{i\}}^{\{n'_k n_k\}}. \quad (6.7)$$

Away from intermediate resonances explicit expressions for the right hand side of Eq.(6.7) may be found from a first principles calculation, but as resonances are approached damping must be considered (§6.2.1). Following the reasoning outlined in §6.1, we incorporate the damping mechanisms contained within the left hand side of Eq.(6.7) into the right hand side via the phenomenological factors $i\Gamma_s$. In a similar fashion to Eq.(6.7) we have

$$\langle \{n_{\bar{k}}\} | \langle \bar{\Psi} | e^{-i\mathcal{H}t/\hbar} | \bar{\Phi} \rangle | \{n'_{\bar{k}}\} \rangle \simeq V_{\{i\}\{f\}}^{\{n_{\bar{k}} n'_{\bar{k}}\}}. \quad (6.8)$$

Hence, by the generalised reversal theorem of Eq.(6.6), we require

$$V_{\{f\}\{i\}}^{\{n'_k n_k\}} = V_{\{i\}\{f\}}^{\{n_{\bar{k}} n'_{\bar{k}}\}}, \quad (6.9)$$

which is equivalent to Eq.(3.27) (see §2.3). We have thus shown that the imaginary addenda must be included into one-particle amplitudes in such a manner as to preserve the reversal theorem (this of course holds true whether the damping factors are found from phenomenological or non-phenomenological arguments). If Eq.(6.9) were not satisfied, the amplitudes would not be a good approximation of the exact amplitudes, i.e. Eq.(6.7) would not hold.

6.2.3 Reciprocity and conjugation theorems

The evolution operator is not invariant under the H and T operations:

$$(e^{-i\mathcal{H}t/\hbar})^\dagger = e^{+i\mathcal{H}t/\hbar} \quad \left(\overline{e^{-i\mathcal{H}t/\hbar}}\right) = e^{+i\mathcal{H}t/\hbar}. \quad (6.10)$$

Hence, the application of these symmetries to Eq.(6.4) does not result in new transition amplitudes:

$$\langle\{n'_k\}|\langle\Phi|e^{-i\mathcal{H}t/\hbar}|\Psi\rangle|\{n_k\}\rangle \stackrel{\text{H}}{=} (\langle\{n_k\}|\langle\Psi|e^{+i\mathcal{H}t/\hbar}|\Phi\rangle|\{n'_k\}\rangle)^*, \quad (6.11)$$

$$\langle\{n'_k\}|\langle\Phi|e^{-i\mathcal{H}t/\hbar}|\Psi\rangle|\{n_k\}\rangle \stackrel{\text{T}}{=} (\langle\{n'_k\}|\langle\bar{\Phi}|e^{+i\mathcal{H}t/\hbar}|\bar{\Psi}\rangle|\{n_k\}\rangle)^*. \quad (6.12)$$

That is, there is no reason to expect the reciprocity and conjugation theorems to relate two physical processes (e.g. the $-\Gamma$ superscripts in Eqs.(3.25) and (3.26)). This result may be contrasted with that in §6.2.2, where it was proven that the reversal theorem always relates two motion-reversed processes (see Eq.(3.27)).

Equations (6.11) and (6.12) are closely related to the discussion of Berger [17], who states that “no special reason is needed for microscopic irreversibility violation” (Berger’s reciprocity violation) and that “microscopic irreversibility is an exception rather than a rule”. Berger [17] lists as one of these exceptions the cases where the interactions are weak so that the amplitude may be found from a Fermi’s Golden Rule approach. It is in this case that we found the reciprocity and conjugation theorems relating two physical processes (i.e. Eqs.(3.25) and (3.26) when the Γ ’s are set to zero).

Note, at the end of §2.1.2 we discussed why we did not include the operation $t \rightarrow -t$ in the time reversal operator. The generalised reversal theorem of Eq.(6.6) provides further support for this choice. In particular, if the operation $t \rightarrow -t$ were incorporated, Eq.(6.6) would no longer relate physical processes since the exponentials on the left and right hand sides of the equation would have opposite signs (as in Eq.(6.10)). It would then be the conjugation theorem that related two physical processes. That is, the amplitudes for motion-reversed processes would no longer be brought into equivalence by the time reversal (i.e. HT) operation.

6.3 Signs of damping factors

In this chapter we are concerned with the signs that are associated with the damping factors. For reasons discussed in §§6.3.1 and 6.3.2, we adopt a prescription where all the signs are identical. This prescription is inequivalent to the most commonly employed prescription. We show that the later violates the reversal theorem (§6.3.3). The two prescriptions can lead to qualitatively different predictions which are particularly amenable to experimental test (§6.4).

6.3.1 Fixed sign prescription

The standard practice for incorporating damping into a theory of light scattering is to include in the energy denominators the phenomenological factors $i\Gamma_s$ (§6.1). In §6.2.2 it was proven that the inclusion of these imaginary addenda must not result in the violation of the reversal theorem. The proof of this theorem requires the energy denominator parts of the amplitude to satisfy

$$D_{fi}^{\pi\{\eta\}\{s\}} = D_{\bar{i}\bar{f}}^{r\{\pi\{-\eta\}\}\{\rho(\bar{s})\}} \quad (6.13)$$

(see §3.1.1). In this section we illustrate the restrictions this equation places on the possible signs that may be associated with the damping factors. We consider in particular the example of second-harmonic generation.

The electronic parts of the transition amplitude for second-harmonic generation are

$$\begin{aligned} \text{Av}_i O_{ii\{0\}}^{\{\alpha,\eta\}} \Big|_{\text{SHG}} = & \text{Av}_i \sum_{s_1, s_2} \frac{\langle i | \mu_{\alpha_3} | s_2 \rangle \langle s_2 | \mu_{\alpha_2} | s_1 \rangle \langle s_1 | \mu_{\alpha_1} | i \rangle}{(E_{i,s_1} + \hbar\omega + \varsigma_1 i\Gamma_{s_1}) (E_{i,s_2} + 2\hbar\omega + \varsigma_2 i\Gamma_{s_2})} \\ & + \frac{\langle i | \mu_{\alpha_2} | s_2 \rangle \langle s_2 | \mu_{\alpha_3} | s_1 \rangle \langle s_1 | \mu_{\alpha_1} | i \rangle}{(E_{i,s_1} + \hbar\omega + \varsigma_3 i\Gamma_{s_1}) (E_{i,s_2} - \hbar\omega + \varsigma_4 i\Gamma_{s_2})} \\ & + \frac{\langle i | \mu_{\alpha_1} | s_2 \rangle \langle s_2 | \mu_{\alpha_2} | s_1 \rangle \langle s_1 | \mu_{\alpha_3} | i \rangle}{(E_{i,s_1} - 2\hbar\omega + \varsigma_5 i\Gamma_{s_1}) (E_{i,s_2} - \hbar\omega + \varsigma_6 i\Gamma_{s_2})}; \end{aligned} \quad (6.14)$$

we assume the electric dipole approximation since higher order multipole couplings do not affect the following discussion. In Eq.(6.14) the $i\Gamma_s$'s have been inserted 'by hand' (§6.1) and the ς 's may be imagined as free parameters that may take on the values ± 1 . For parametric down-conversion the electronic parts are

$$\begin{aligned} \text{Av}_i O_{ii\{0\}}^{\{\alpha,\eta\}} \Big|_{\text{PDC}} = & \text{Av}_i \sum_{s_1, s_2} \frac{\langle i | \mu_{\alpha_3} | s_2 \rangle \langle s_2 | \mu_{\alpha_2} | s_1 \rangle \langle s_1 | \mu_{\alpha_1} | i \rangle}{(E_{i,s_1} - \hbar\omega + \varsigma'_1 i\Gamma_{s_1}) (E_{i,s_2} - 2\hbar\omega + \varsigma'_2 i\Gamma_{s_2})} \\ & + \frac{\langle i | \mu_{\alpha_2} | s_2 \rangle \langle s_2 | \mu_{\alpha_3} | s_1 \rangle \langle s_1 | \mu_{\alpha_1} | i \rangle}{(E_{i,s_1} - \hbar\omega + \varsigma'_3 i\Gamma_{s_1}) (E_{i,s_2} + \hbar\omega + \varsigma'_4 i\Gamma_{s_2})} \\ & + \frac{\langle i | \mu_{\alpha_1} | s_2 \rangle \langle s_2 | \mu_{\alpha_2} | s_1 \rangle \langle s_1 | \mu_{\alpha_3} | i \rangle}{(E_{i,s_1} + 2\hbar\omega + \varsigma'_5 i\Gamma_{s_1}) (E_{i,s_2} + \hbar\omega + \varsigma'_6 i\Gamma_{s_2})}, \end{aligned} \quad (6.15)$$

where the primes allow for different ς 's in this process. In order for Eqs.(6.14) and (6.15) to be equivalent under HT, i.e. by Eq.(6.13), we require

$$\varsigma'_j = \varsigma_{6-j+1} \quad j = 1, \dots, 6 \quad (6.16)$$

(similar conditions are found when other nonlinear optical processes are considered). Note, as discussed in §3.1.1, the derivation of Eqs.(6.13) and (6.16) requires the relation $\Gamma_s = \Gamma_{\bar{s}}$. This is proved in Andrews *et al.* [8] by an application of HT symmetry to the imaginary parts of the Brillouin-Wigner perturbative expansion of the self-energy.

Equation (6.16) has many solutions, i.e. time reversal symmetry alone cannot completely specify the ς 's. The simplest solution to Eq.(6.16) is $\varsigma_j = \varsigma'_j = 1$ for all j . For reasons discussed in §6.3.2, this is the solution we adopt for this and all other processes (see Eq.(2.18)). Other workers who also arrive at this fixed sign prescription are Hecht and Barron [61] (who cite Weisskopf [138]) for Rayleigh and Raman scattering and Mazely and Hetherington [98] second-harmonic generation. Incidentally, this choice of signs amounts to replacing the excited state energies E_s by the complex quantity $E_s - i\Gamma_s$ [13].

6.3.2 Non-phenomenological approaches

As discussed in §6.1, an analysis of damping based on a first principles calculation is generally intractable. However, as we now briefly review, in a few cases a non-phenomenological approach is possible.

Cohen-Tannoudji *et al.* [34] consider radiative damping for resonant Rayleigh scattering by a single molecule. In their non-perturbative approach they employ the resolvent operator method to sum appropriate diagrams to infinite order. These infinite sums enter into the energy denominators in exactly the same fashion as we have discussed for phenomenological damping. In particular, the resulting transition amplitude is [34]

$$O_{fi\{0\}}^{\{\alpha,\eta\}} \Big|_{\text{RS}} = \sum_s \frac{\langle f | \mu_{\alpha_2} | s \rangle \langle s | \mu_{\alpha_1} | i \rangle}{E_{i,s} + \hbar\omega + i\Gamma_s} + \frac{\langle f | \mu_{\alpha_1} | s \rangle \langle s | \mu_{\alpha_2} | i \rangle}{E_{i,s} - \hbar\omega + i\Gamma_s}, \quad (6.17)$$

i.e. takes the same form as the amplitude given in Eq.(2.32). Cohen-Tannoudji *et al.* [34] show that for radiative damping Γ_s is the sum of the one-photon transition rates from the level s to all other levels (and hence satisfies $\Gamma_s = \Gamma_{\bar{s}}$). For this simple system of a single molecule in a radiation field it may be possible to extend this Rayleigh scattering calculation to cover second-harmonic generation, and therefore prove in detail whether the fixed sign prescription is also appropriate for that process. This is not attempted here.

Equation (6.17) is consistent with the closely related application of quantum field theoretical methods of statistical physics to electronic spectra [99, 126]. As discussed in Andrews *et al.* [8], the many-body formalism given in, for example, Refs. [99, 126] may in principle be used to determine the signs of the damping factors. A first step along these lines was taken in Andrews *et al.* [8] and it was concluded that the signs should all be identical. Because of this, and because of Eq.(6.17), we adopted the fixed sign prescription in §6.3.1.

6.3.3 Time-Ordered sign prescription

In §§6.3.1 and 6.3.2 we presented our reasoning for choosing the fixed sign prescription. We now discuss another prescription, which we term the time-ordered

sign prescription, where the signs of the damping factors vary according to the temporal ordering of the associated photon interactions. This prescription is usually associated with the optical susceptibility formalism (outlined in §2.2.2), and is often employed. We show, however, that it is inconsistent with the analyses in §§6.3.1 and 6.3.2.

Butcher *et al.* [24] and Butcher and Cotter [23] (see also Ref. [59]) choose the signs of their damping addenda by requiring that in the evaluation of the optical susceptibility tensors time integrals should converge. For the generation of optical harmonics and in the susceptibility contribution corresponding to each time-ordering, these damping terms then carry opposite signs for interactions preceding and following emission of the harmonic photon (see Eqs.(6.18) and (6.20)). Bloembergen [19], Flytzanis [41], Shen [121] and Levenson and Kano [87] for example implement damping at the density matrix level and derive susceptibilities with a similar assignment of signs but with extra term added. Here we need not distinguish these two susceptibility expressions as only the signs of the damping addenda are examined in this chapter.

The lowest order susceptibility is associated with coherent Rayleigh scattering and in the electric dipole approximation takes the form [23]

$$\chi_{\alpha_2\alpha_1}^{(1)}(-\omega; \omega) = \sum_i e^{-E_i/kT} \sum_s \frac{\langle i|\mu_{\alpha_2}|s\rangle\langle s|\mu_{\alpha_1}|i\rangle}{E_{i,s} + \hbar\omega + i\Gamma_s} + \frac{\langle i|\mu_{\alpha_1}|s\rangle\langle s|\mu_{\alpha_2}|i\rangle}{E_{i,s} - \hbar\omega - i\Gamma_s}, \quad (6.18)$$

the phenomenological factors $i\Gamma_s$ model the combination of all damping mechanisms (as in §6.3.1). The optical susceptibility tensors must give the amplitude of the light scattering intensity [87]. However, the amplitude given by Eq.(6.18) is inequivalent to that given in Eqs.(2.32) and (6.17). In particular, there is a -1 associated with the imaginary addendum in the second term of Eq.(6.18)

Equation (6.18) violates the reversal theorem proven in §6.2.2. In particular, the application of HT symmetry to Eq.(6.18) gives

$$\begin{aligned} \chi_{\alpha_2\alpha_1}^{(1)}(-\omega; \omega) &= \sum_i e^{-E_i/kT} \sum_s \frac{\langle i|\mu_{\alpha_1}|s\rangle\langle s|\mu_{\alpha_2}|i\rangle}{E_{i,s} + \hbar\omega + i\Gamma_s} + \frac{\langle i|\mu_{\alpha_2}|s\rangle\langle s|\mu_{\alpha_1}|i\rangle}{E_{i,s} - \hbar\omega - i\Gamma_s} \\ &\neq \chi_{\alpha_1\alpha_2}^{(1)}(\omega; -\omega). \end{aligned} \quad (6.19)$$

Following a similar analysis as in §6.3.1, it is readily seen that time reversal symmetry requires the signs of the two damping addenda to be identical as in Eq.(6.17), rather than opposite as in Eq.(6.18).

We now show that in the time-ordered sign prescription the reversal theorem is also violated for the example of second-harmonic generation. The associated susceptibility tensor, obtained by reference to the methods of Butcher and

Cotter [23], is of the form

$$\begin{aligned} \chi_{\alpha_3\alpha_2\alpha_1}^{(2)}(-2\omega; \omega, \omega) = & \sum_i e^{-E_i/kT} \sum_{s_1, s_2} \frac{\langle i|\mu_{\alpha_3}|s_2\rangle \langle s_2|\mu_{\alpha_2}|s_1\rangle \langle s_1|\mu_{\alpha_1}|i\rangle}{(E_{i,s_1} + \hbar\omega + i\Gamma_{s_1})(E_{i,s_2} + 2\hbar\omega + i\Gamma_{s_2})} \\ & + \frac{\langle i|\mu_{\alpha_2}|s_2\rangle \langle s_2|\mu_{\alpha_3}|s_1\rangle \langle s_1|\mu_{\alpha_1}|i\rangle}{(E_{i,s_1} + \hbar\omega + i\Gamma_{s_1})(E_{i,s_2} - \hbar\omega - i\Gamma_{s_2})} \\ & + \frac{\langle i|\mu_{\alpha_1}|s_2\rangle \langle s_2|\mu_{\alpha_2}|s_1\rangle \langle s_1|\mu_{\alpha_3}|i\rangle}{(E_{i,s_1} - 2\hbar\omega - i\Gamma_{s_1})(E_{i,s_2} - \hbar\omega - i\Gamma_{s_2})}. \end{aligned} \quad (6.20)$$

The application of HT symmetry gives

$$\begin{aligned} \chi_{\alpha_3\alpha_2\alpha_1}^{(2)}(-2\omega; \omega, \omega) = & \sum_i e^{-E_i/kT} \sum_{s_1, s_2} \frac{\langle i|\mu_{\alpha_3}|s_2\rangle \langle s_2|\mu_{\alpha_2}|s_1\rangle \langle s_1|\mu_{\alpha_1}|i\rangle}{(E_{i,s_1} - \hbar\omega - i\Gamma_{s_1})(E_{i,s_2} - 2\hbar\omega - i\Gamma_{s_2})} \\ & + \frac{\langle i|\mu_{\alpha_1}|s_2\rangle \langle s_2|\mu_{\alpha_3}|s_1\rangle \langle s_1|\mu_{\alpha_2}|i\rangle}{(E_{i,s_1} - \hbar\omega - i\Gamma_{s_1})(E_{i,s_2} + \hbar\omega + i\Gamma_{s_2})} \\ & + \frac{\langle i|\mu_{\alpha_1}|s_2\rangle \langle s_2|\mu_{\alpha_2}|s_1\rangle \langle s_1|\mu_{\alpha_3}|i\rangle}{(E_{i,s_1} + 2\hbar\omega + i\Gamma_{s_1})(E_{i,s_2} + \hbar\omega + i\Gamma_{s_2})}, \end{aligned} \quad (6.21)$$

whereas

$$\begin{aligned} \chi_{\alpha_3\alpha_2\alpha_1}^{(2)}(2\omega; -\omega, -\omega) = & \sum_i e^{-E_i/kT} \sum_{s_1, s_2} \frac{\langle i|\mu_{\alpha_3}|s_2\rangle \langle s_2|\mu_{\alpha_2}|s_1\rangle \langle s_1|\mu_{\alpha_1}|i\rangle}{(E_{i,s_1} - \hbar\omega + i\Gamma_{s_1})(E_{i,s_2} - 2\hbar\omega + i\Gamma_{s_2})} \\ & + \frac{\langle i|\mu_{\alpha_2}|s_2\rangle \langle s_2|\mu_{\alpha_3}|s_1\rangle \langle s_1|\mu_{\alpha_1}|i\rangle}{(E_{i,s_1} - \hbar\omega + i\Gamma_{s_1})(E_{i,s_2} + \hbar\omega - i\Gamma_{s_2})} \\ & + \frac{\langle i|\mu_{\alpha_1}|s_2\rangle \langle s_2|\mu_{\alpha_2}|s_1\rangle \langle s_1|\mu_{\alpha_3}|i\rangle}{(E_{i,s_1} + 2\hbar\omega - i\Gamma_{s_1})(E_{i,s_2} + \hbar\omega - i\Gamma_{s_2})}. \end{aligned} \quad (6.22)$$

That is,

$$\chi_{\alpha_3\alpha_2\alpha_1}^{(2)}(-2\omega; \omega, \omega) \neq \chi_{\alpha_3\alpha_2\alpha_1}^{(2)}(2\omega; -\omega, -\omega), \quad (6.23)$$

because the $i\Gamma$'s are of opposite signs in Eqs.(6.21) and (6.22). This type of inequivalence exists between all other T-conjugate processes in the time-ordered sign prescription.

We have shown that the phenomenological damping approach involving the time-ordered sign prescription violates the reversal theorem proved in §6.2.2. This is true regardless of the exact damping mechanisms present. Indeed, on page 88 Flytzanis [41] states without justification that "...time-reversal symmetry properties break down when damping is included". We may thus conclude that this commonly employed scheme, usually associated with the optical susceptibility formalism, is inaccurate. This statement does not require a first principles calculation of the type discussed in §6.3.2, but is based on symmetry considerations.

In the absence of damping factors the second-harmonic generation amplitude is invariant under the permutations

$$(\alpha_j, \eta_j) \leftrightarrow (\alpha_{j'}, \eta_{j'}), \quad (6.24)$$

where the indices j, j' run over the three participating photons (see for example Butcher and Cotter [23]). This symmetry is referred to as overall permutation symmetry. When damping factors are included this symmetry continues to hold in the fixed sign prescription but no longer holds in the time-ordered sign prescription. Because all temporal orderings are summed over, Eq.(6.24) should hold regardless of presence of damping. This provides further support for the fixed sign prescription.

It may be asked then, why it is that the susceptibility description of nonlinear optics is inaccurate. First, the various analyses of transition amplitudes referred to in §6.3.2, based as they are on resolvent or field theoretic techniques, directly calculate the observables of quantum theory. The susceptibility formulation has a semiclassical foundation and derives from a tradition long established in classical optics, wherein a material polarisation is regarded as the source of any emergent signal. Second, the description of optical response in terms of susceptibility, whether linear or nonlinear, is arguably inappropriate [6, 8]. For example it leads to the obviously false conclusion that any system exposed to even one photon can, through quadratic interaction mediated by a second order susceptibility, weakly generate second harmonic output [8]. We therefore believe that the proper formulation of any optical process requires its expression in terms of direct observables, principally rates and signal intensities, rather than the (at best) inferred optical susceptibilities.

Finally we note that under hermitian conjugation H Eq.(6.20) transforms as

$$\begin{aligned} \chi_{\alpha_3\alpha_2\alpha_1}^{(2)}(-2\omega; \omega, \omega) = \sum_i e^{-E_i/kT} \sum_{s_1, s_2} \left\{ \frac{\langle i|\mu_{\alpha_1}|s_2\rangle \langle s_2|\mu_{\alpha_2}|s_1\rangle \langle s_1|\mu_{\alpha_3}|i\rangle}{(E_{i,s_1} + 2\hbar\omega - i\Gamma_{s_1})(E_{i,s_2} + \hbar\omega - i\Gamma_{s_2})} \right. \\ + \frac{\langle i|\mu_{\alpha_1}|s_2\rangle \langle s_2|\mu_{\alpha_3}|s_1\rangle \langle s_1|\mu_{\alpha_2}|i\rangle}{(E_{i,s_1} - \hbar\omega + i\Gamma_{s_1})(E_{i,s_2} + \hbar\omega - i\Gamma_{s_2})} \\ \left. + \frac{\langle i|\mu_{\alpha_3}|s_2\rangle \langle s_2|\mu_{\alpha_2}|s_1\rangle \langle s_1|\mu_{\alpha_1}|i\rangle}{(E_{i,s_1} - \hbar\omega + i\Gamma_{s_1})(E_{i,s_2} - 2\hbar\omega + i\Gamma_{s_2})} \right\}^*, \quad (6.25) \end{aligned}$$

so that in the time-ordered sign prescription the reciprocity theorem relates two physical processes:

$$\{\chi_{\alpha_3\alpha_2\alpha_1}^{(2)}(-2\omega; \omega, \omega)\}^* = \chi_{\alpha_3\alpha_2\alpha_1}^{(2)}(2\omega; -\omega, -\omega). \quad (6.26)$$

In the standard semiclassical susceptibility theory any process must satisfy this type of relation in order for the Fourier transform and so the polarisation to be a real quantity [23]. It has been explicitly demonstrated in Eq.(3.35) that in the fixed sign prescription the amplitude does not satisfy Eq.(6.26). However, as discussed in §6.2.3, the reciprocity relation of Eq.(6.26) need not hold in general, and hence does not constitute support for the time-ordered sign prescription.

6.4 Experimental test: Electrooptic rotation

The second-harmonic intensity expressions are given by $|\chi_{\alpha_3\alpha_2\alpha_1}^{(2)}(-2\omega; \omega, \omega)|^2$ and $|\text{Av}_i O_{ii\{0\}}^{\{\alpha, \eta\}}|_{\text{SHG}}|^2$ in the time-ordered and fixed sign formulations respectively. When damping is included Eqs.(6.20) and (2.39) show that $\chi_{\alpha_3\alpha_2\alpha_1}^{(2)}(-2\omega; \omega, \omega)$ and $\text{Av}_i O_{ii\{0\}}^{\{\alpha, \eta\}}|_{\text{SHG}}$ are not proportional, nor do they stand in a complex conjugate relationship:

$$|\chi_{\alpha_3\alpha_2\alpha_1}^{(2)}(-2\omega; \omega, \omega)|^2 \neq |O_{fi\{0\}}^{\{\alpha, \eta\}}|_{\text{SHG}}|^2. \quad (6.27)$$

Therefore those alternative formulations lead to intensity expressions that in principle are physically distinguishable. The denominator factors of $\chi_{\alpha_3\alpha_2\alpha_1}^{(2)}(-2\omega; \omega, \omega)$ that may be resonant have the correct positive imaginary parts; only the ‘anti-resonant’ factors have negative imaginary parts (compare Eqs.(6.20) and (2.39)). Hence the difference between results cast in terms of $\chi_{\alpha_3\alpha_2\alpha_1}^{(2)}(-2\omega; \omega, \omega)$ and $\text{Av}_i O_{ii\{0\}}^{\{\alpha, \eta\}}|_{\text{SHG}}$ is generally likely to be small in applications and an experimental test of Eq.(6.27) via a direct measurement of scattering intensities is unlikely to be successful. At this level of discussion the importance of these corrections might be judged to be similar to that of departures from the rotating wave approximation, which itself depends on retaining only resonant terms.

To find realistic experimental tests of Eq.(6.27) we must consider situations where the time-ordered sign prescription leads to predictions that are qualitatively different from those found in the fixed sign prescription. Ideal candidates are those processes which highlight the time reversal violation of the time-ordered formulation. As described below, the coherent process of electrooptic rotation (forward Rayleigh scattering between orthogonal linear polarisations in the presence of an external electric field) in fluid media is an example of such a process.

The amplitudes for electrooptic rotation in the time-ordered and fixed sign prescriptions are respectively

$$\begin{aligned} \chi_{\alpha_3\alpha_2\alpha_1}^{(2)}(-\omega; \omega, 0) = & \sum_i e^{-E_i/kT} \sum_{s_1, s_2} \frac{\langle i|\mu_{\alpha_3}|s_2\rangle\langle s_2|\mu_{\alpha_2}|s_1\rangle\langle s_1|\mu_{\alpha_1}|i\rangle}{(E_{i,s_1} + i\Gamma_{s_1})(E_{i,s_2} + \hbar\omega + i\Gamma_{s_2})} + \frac{\langle i|\mu_{\alpha_1}|s_2\rangle\langle s_2|\mu_{\alpha_3}|s_1\rangle\langle s_1|\mu_{\alpha_2}|i\rangle}{(E_{i,s_1} + \hbar\omega + i\Gamma_{s_1})(E_{i,s_2} - i\Gamma_{s_2})} \\ & + \frac{\langle i|\mu_{\alpha_2}|s_2\rangle\langle s_2|\mu_{\alpha_1}|s_1\rangle\langle s_1|\mu_{\alpha_3}|i\rangle}{(E_{i,s_1} - \hbar\omega - i\Gamma_{s_1})(E_{i,s_2} - \hbar\omega - i\Gamma_{s_2})} + \frac{\langle i|\mu_{\alpha_3}|s_2\rangle\langle s_2|\mu_{\alpha_1}|s_1\rangle\langle s_1|\mu_{\alpha_2}|i\rangle}{(E_{i,s_1} + \hbar\omega + i\Gamma_{s_1})(E_{i,s_2} + \hbar\omega + i\Gamma_{s_2})} \\ & + \frac{\langle i|\mu_{\alpha_2}|s_2\rangle\langle s_2|\mu_{\alpha_3}|s_1\rangle\langle s_1|\mu_{\alpha_1}|i\rangle}{(E_{i,s_1} + i\Gamma_{s_1})(E_{i,s_2} - \hbar\omega - i\Gamma_{s_2})} + \frac{\langle i|\mu_{\alpha_1}|s_2\rangle\langle s_2|\mu_{\alpha_2}|s_1\rangle\langle s_1|\mu_{\alpha_3}|i\rangle}{(E_{i,s_1} - \hbar\omega - i\Gamma_{s_1})(E_{i,s_2} - i\Gamma_{s_2})}, \quad (6.28) \end{aligned}$$

$$\begin{aligned}
O_{fi\{0\}}^{\{\alpha,\eta\}} \Big|_{\text{EOR}} = & \\
& \text{AV} \sum_{i, s_1, s_2} \frac{\langle i | \mu_{\alpha_3} | s_2 \rangle \langle s_2 | \mu_{\alpha_2} | s_1 \rangle \langle s_1 | \mu_{\alpha_1} | i \rangle}{(E_{i, s_1} + i\Gamma_{s_1})(E_{i, s_2} + \hbar\omega + i\Gamma_{s_2})} + \frac{\langle i | \mu_{\alpha_1} | s_2 \rangle \langle s_2 | \mu_{\alpha_3} | s_1 \rangle \langle s_1 | \mu_{\alpha_2} | i \rangle}{(E_{i, s_1} + \hbar\omega + i\Gamma_{s_1})(E_{i, s_2} + i\Gamma_{s_2})} \\
& + \frac{\langle i | \mu_{\alpha_2} | s_2 \rangle \langle s_2 | \mu_{\alpha_1} | s_1 \rangle \langle s_1 | \mu_{\alpha_3} | i \rangle}{(E_{i, s_1} - \hbar\omega + i\Gamma_{s_1})(E_{i, s_2} - \hbar\omega + i\Gamma_{s_2})} + \frac{\langle i | \mu_{\alpha_3} | s_2 \rangle \langle s_2 | \mu_{\alpha_1} | s_1 \rangle \langle s_1 | \mu_{\alpha_2} | i \rangle}{(E_{i, s_1} + \hbar\omega + i\Gamma_{s_1})(E_{i, s_2} + \hbar\omega + i\Gamma_{s_2})} \\
& + \frac{\langle i | \mu_{\alpha_2} | s_2 \rangle \langle s_2 | \mu_{\alpha_3} | s_1 \rangle \langle s_1 | \mu_{\alpha_1} | i \rangle}{(E_{i, s_1} + i\Gamma_{s_1})(E_{i, s_2} - \hbar\omega + i\Gamma_{s_2})} + \frac{\langle i | \mu_{\alpha_1} | s_2 \rangle \langle s_2 | \mu_{\alpha_2} | s_1 \rangle \langle s_1 | \mu_{\alpha_3} | i \rangle}{(E_{i, s_1} - \hbar\omega + i\Gamma_{s_1})(E_{i, s_2} + i\Gamma_{s_2})}. \quad (6.29)
\end{aligned}$$

The application of HT symmetry to the second, third, fourth and sixth terms in these two amplitudes gives

$$\begin{aligned}
\chi_{\alpha_3 \alpha_2 \alpha_1}^{(2)}(-\omega; \omega, 0) = & \\
& \sum_i e^{-E_i/kT} \sum_{s_1, s_2} \frac{\langle i | \mu_{\alpha_3} | s_2 \rangle \langle s_2 | \mu_{\alpha_2} | s_1 \rangle \langle s_1 | \mu_{\alpha_1} | i \rangle}{(E_{i, s_1} + i\Gamma_{s_1})(E_{i, s_2} + \hbar\omega + i\Gamma_{s_2})} + \frac{\langle i | \mu_{\alpha_2} | s_2 \rangle \langle s_2 | \mu_{\alpha_3} | s_1 \rangle \langle s_1 | \mu_{\alpha_1} | i \rangle}{(E_{i, s_1} - i\Gamma_{s_1})(E_{i, s_2} + \hbar\omega + i\Gamma_{s_2})} \\
& + \frac{1}{2} \frac{\langle i | \mu_{\alpha_2} | s_2 \rangle \langle s_2 | \mu_{\alpha_1} | s_1 \rangle \langle s_1 | \mu_{\alpha_3} | i \rangle + \langle i | \mu_{\alpha_3} | s_2 \rangle \langle s_2 | \mu_{\alpha_1} | s_1 \rangle \langle s_1 | \mu_{\alpha_2} | i \rangle}{(E_{i, s_1} - \hbar\omega - i\Gamma_{s_1})(E_{i, s_2} - \hbar\omega - i\Gamma_{s_2})} \\
& + \frac{1}{2} \frac{\langle i | \mu_{\alpha_3} | s_2 \rangle \langle s_2 | \mu_{\alpha_1} | s_1 \rangle \langle s_1 | \mu_{\alpha_2} | i \rangle + \langle i | \mu_{\alpha_2} | s_2 \rangle \langle s_2 | \mu_{\alpha_1} | s_1 \rangle \langle s_1 | \mu_{\alpha_3} | i \rangle}{(E_{i, s_1} + \hbar\omega + i\Gamma_{s_1})(E_{i, s_2} + \hbar\omega + i\Gamma_{s_2})} \\
& + \frac{\langle i | \mu_{\alpha_2} | s_2 \rangle \langle s_2 | \mu_{\alpha_3} | s_1 \rangle \langle s_1 | \mu_{\alpha_1} | i \rangle}{(E_{i, s_1} + i\Gamma_{s_1})(E_{i, s_2} - \hbar\omega - i\Gamma_{s_2})} + \frac{\langle i | \mu_{\alpha_3} | s_2 \rangle \langle s_2 | \mu_{\alpha_2} | s_1 \rangle \langle s_1 | \mu_{\alpha_1} | i \rangle}{(E_{i, s_1} - i\Gamma_{s_1})(E_{i, s_2} - \hbar\omega - i\Gamma_{s_2})}, \quad (6.30)
\end{aligned}$$

$$\begin{aligned}
O_{fi\{0\}}^{\{\alpha,\eta\}} \Big|_{\text{EOR}} = & \\
& \text{AV} \sum_i \frac{\langle i | \mu_{\alpha_3} | s_2 \rangle \langle s_2 | \mu_{\alpha_2} | s_1 \rangle \langle s_1 | \mu_{\alpha_1} | i \rangle}{(E_{i, s_1} + i\Gamma_{s_1})(E_{i, s_2} + \hbar\omega + i\Gamma_{s_2})} + \frac{\langle i | \mu_{\alpha_2} | s_2 \rangle \langle s_2 | \mu_{\alpha_3} | s_1 \rangle \langle s_1 | \mu_{\alpha_1} | i \rangle}{(E_{i, s_1} + i\Gamma_{s_1})(E_{i, s_2} + \hbar\omega + i\Gamma_{s_2})} \\
& + \frac{1}{2} \frac{\langle i | \mu_{\alpha_2} | s_2 \rangle \langle s_2 | \mu_{\alpha_1} | s_1 \rangle \langle s_1 | \mu_{\alpha_3} | i \rangle + \langle i | \mu_{\alpha_3} | s_2 \rangle \langle s_2 | \mu_{\alpha_1} | s_1 \rangle \langle s_1 | \mu_{\alpha_2} | i \rangle}{(E_{i, s_1} - \hbar\omega + i\Gamma_{s_1})(E_{i, s_2} - \hbar\omega + i\Gamma_{s_2})} \\
& + \frac{1}{2} \frac{\langle i | \mu_{\alpha_3} | s_2 \rangle \langle s_2 | \mu_{\alpha_1} | s_1 \rangle \langle s_1 | \mu_{\alpha_2} | i \rangle + \langle i | \mu_{\alpha_2} | s_2 \rangle \langle s_2 | \mu_{\alpha_1} | s_1 \rangle \langle s_1 | \mu_{\alpha_3} | i \rangle}{(E_{i, s_1} + \hbar\omega + i\Gamma_{s_1})(E_{i, s_2} + \hbar\omega + i\Gamma_{s_2})} \\
& + \frac{\langle i | \mu_{\alpha_2} | s_2 \rangle \langle s_2 | \mu_{\alpha_3} | s_1 \rangle \langle s_1 | \mu_{\alpha_1} | i \rangle}{(E_{i, s_1} + i\Gamma_{s_1})(E_{i, s_2} - \hbar\omega + i\Gamma_{s_2})} + \frac{\langle i | \mu_{\alpha_3} | s_2 \rangle \langle s_2 | \mu_{\alpha_2} | s_1 \rangle \langle s_1 | \mu_{\alpha_1} | i \rangle}{(E_{i, s_1} + i\Gamma_{s_1})(E_{i, s_2} - \hbar\omega + i\Gamma_{s_2})}. \quad (6.31)
\end{aligned}$$

We thus see that $O_{fi\{0\}}^{\{\alpha,\eta\}} \Big|_{\text{EOR}}$ but not $\chi_{\alpha_3 \alpha_2 \alpha_1}^{(2)}(-\omega; \omega, 0)$ is symmetric under the interchange $\alpha_3 \leftrightarrow \alpha_2$.

In a fluid we detect only the rotationally invariant part, and must contract these tensors with the Levi-Civita symbol $\epsilon_{\alpha_3 \alpha_2 \alpha_1}$ (see for example Ref. [9]). However such an antisymmetric combination is incompatible with the index symmetry of the amplitude in the fixed sign prescription. Hence, in the correct formulation this process is forbidden, whereas it is allowed under the popular alternative sign choice (i.e. there is a qualitative difference in prediction between the two prescriptions).

To estimate the magnitude of the electrooptic rotation in the time-ordered sign prescription we require the parts of $\chi_{\alpha_3\alpha_2\alpha_1}^{(2)}(-\omega; \omega, 0)$ that are antisymmetric under the interchange $\alpha_3 \leftrightarrow \alpha_2$:

$$\begin{aligned} \frac{1}{2} (\chi_{\alpha_3\alpha_2\alpha_1}^{(2)}(-\omega; \omega, 0) - \chi_{\alpha_2\alpha_3\alpha_1}^{(2)}(-\omega; \omega, 0)) = \sum_i e^{-E_i/kT} \sum_{s_1, s_2} \frac{-i\Gamma_{s_1}}{E_{i,s_1}^2 + \Gamma_{s_1}^2} \times \\ \left\{ \frac{\langle i|\mu_{\alpha_3}|s_2\rangle\langle s_2|\mu_{\alpha_2}|s_1\rangle\langle s_1|\mu_{\alpha_1}|i\rangle - \langle i|\mu_{\alpha_1}|s_1\rangle\langle s_1|\mu_{\alpha_3}|s_2\rangle\langle s_2|\mu_{\alpha_2}|i\rangle}{E_{i,s_2} + \hbar\omega + i\Gamma_{s_2}} \right. \\ \left. + \frac{\langle i|\mu_{\alpha_2}|s_2\rangle\langle s_2|\mu_{\alpha_3}|s_1\rangle\langle s_1|\mu_{\alpha_1}|i\rangle - \langle i|\mu_{\alpha_1}|s_1\rangle\langle s_1|\mu_{\alpha_2}|s_2\rangle\langle s_2|\mu_{\alpha_3}|i\rangle}{E_{i,s_2} - \hbar\omega - i\Gamma_{s_2}} \right\}. \quad (6.32) \end{aligned}$$

The effect is therefore of order $\Gamma_s/E_{i,s}$ times the amplitude. In the fixed sign prescription the process is allowed at multipole couplings beyond the electric dipole approximation. We now compare the magnitudes of these allowed terms with Eq.(6.32) to estimate whether an experiment may distinguish between the two prescriptions.

We denote the polarisation of the static electric field by \mathbf{e}_s , and denote the polarisations of the incoming and outgoing photons by \mathbf{e}_1 and \mathbf{e}_2 respectively (both with wavevector \mathbf{k}). In the electric dipole approximation the rotational average results in these three vectors contracting to give the scalar $(\mathbf{e}_2 \times \mathbf{e}_1) \cdot \mathbf{e}_s$ [9]; \mathbf{e}_s therefore must have a projection along \mathbf{k} . At the magnetic dipole and electric quadrupole level, i.e. at the level that is linear in \mathbf{k} , the rotational average results in the three scalars [9]

$$(\mathbf{e}_2 \cdot \mathbf{e}_1)(\mathbf{e}_s \cdot \mathbf{k}), \quad (\mathbf{e}_2 \cdot \mathbf{e}_s)(\mathbf{e}_1 \cdot \mathbf{k}), \quad (\mathbf{e}_1 \cdot \mathbf{e}_s)(\mathbf{e}_2 \cdot \mathbf{k}), \quad (6.33)$$

all three of which are necessarily zero. For the parts of the amplitude that are quadratic in \mathbf{k} the rotational average results in scalars such as [9] $(\mathbf{e}_2 \times \mathbf{e}_1) \cdot \mathbf{e}_s(\mathbf{k} \cdot \mathbf{k})$, which are nonzero for any choice of polarisations. The process is therefore possible at this level in the fixed sign prescription. Supposing that this level is approximately $(137)^{-2}$ times the electric dipole amplitude, the ratio of the amplitudes in the two prescriptions is

$$\frac{\text{time-ordered signs}}{\text{fixed signs}} \simeq (137)^2 \frac{\Gamma_s}{E_{i,s}}. \quad (6.34)$$

To distinguish between the two cases we require the magnitude of the effect in the time-ordered sign prescription to be clearly larger than the effect in the fixed sign prescription. That is, we require $\Gamma_s/E_{i,s}$ to be clearly larger than $(137)^{-2}$. Loudon [94] gives $\Gamma_s/\hbar \simeq 10^{11}$ for collisional damping and Butcher and Cotter [23] give $E_{i,s}/\hbar \simeq 10^{15}$ (both in units of per second). The ratio in Eq.(6.34) is therefore of order unity. Hence, the experiment is feasible, but not for any system. In particular, a material subsystem is required where the damping is at least an order of magnitude larger than collisional damping (or $E_{i,s}/\hbar \simeq 10^{14}$).

Finally, we note that the circular intensity difference analysis of Chap. 5 cannot be used to distinguish between the two prescriptions, even though that discussion

hinged on the inclusion of damping factors. In particular, under the T operation we have

$$\begin{aligned} \chi_{\alpha_3\alpha_2\alpha_1}^{(2)}(-\omega; \omega, 0) = & \sum_i e^{-E_i/kT} \sum_{s_1, s_2} \\ & \left\{ \frac{\langle i|\mu_{\alpha_3}|s_2\rangle\langle s_2|\mu_{\alpha_2}|s_1\rangle\langle s_1|\mu_{\alpha_1}|i\rangle}{(E_{i,s_1} - i\Gamma_{s_1})(E_{i,s_2} + \hbar\omega - i\Gamma_{s_2})} + \frac{\langle i|\mu_{\alpha_1}|s_2\rangle\langle s_2|\mu_{\alpha_3}|s_1\rangle\langle s_1|\mu_{\alpha_2}|i\rangle}{(E_{i,s_1} + \hbar\omega - i\Gamma_{s_1})(E_{i,s_2} + i\Gamma_{s_2})} \right. \\ & + \frac{\langle i|\mu_{\alpha_2}|s_2\rangle\langle s_2|\mu_{\alpha_1}|s_1\rangle\langle s_1|\mu_{\alpha_3}|i\rangle}{(E_{i,s_1} - \hbar\omega + i\Gamma_{s_1})(E_{i,s_2} - \hbar\omega + i\Gamma_{s_2})} + \frac{\langle i|\mu_{\alpha_3}|s_2\rangle\langle s_2|\mu_{\alpha_1}|s_1\rangle\langle s_1|\mu_{\alpha_2}|i\rangle}{(E_{i,s_1} + \hbar\omega - i\Gamma_{s_1})(E_{i,s_2} + \hbar\omega - i\Gamma_{s_2})} \\ & \left. + \frac{\langle i|\mu_{\alpha_2}|s_2\rangle\langle s_2|\mu_{\alpha_3}|s_1\rangle\langle s_1|\mu_{\alpha_1}|i\rangle}{(E_{i,s_1} - i\Gamma_{s_1})(E_{i,s_2} - \hbar\omega + i\Gamma_{s_2})} + \frac{\langle i|\mu_{\alpha_1}|s_2\rangle\langle s_2|\mu_{\alpha_2}|s_1\rangle\langle s_1|\mu_{\alpha_3}|i\rangle}{(E_{i,s_1} - \hbar\omega + i\Gamma_{s_1})(E_{i,s_2} + i\Gamma_{s_2})} \right\}^* \quad (6.35) \end{aligned}$$

which, upon complex conjugation, differs from the original amplitude by the change of sign of all the imaginary addenda $i\Gamma_s$ (an identical result holds for all other processes). This is precisely the same relation as exists in the fixed sign prescription (Eq.(3.12)). That is, the intensity difference expression of Eqs.(5.1) and (5.5) takes the same form in both the prescriptions.

7. Effective transition operator parameterisation

This short chapter reports on a work in progress. The results described below highlight issues worthy of further investigation; these will be addressed in the future (as described in §7.3).

7.1 Introduction

In 1962 Judd [68] and Ofelt [108] provided a parameterisation of one photon absorption intensities within the $4f^n$ configuration of lanthanide ions in solids. This Judd-Ofelt theory has since received much attention (see for example Reid [116] for a review). The theory involves expressing the transition amplitude as a matrix element of an effective operator and expanding this operator as a sum of spherical tensors. A key aspect is the demonstration that these spherical tensors are of even rank. Judd [68] and Ofelt [108] proved this under the assumption of degeneracy and closure approximations (the degeneracy approximation is analogous to taking the nonresonant limit and the closure approximation supposes the energies of the excited multiplet may be taken as identical). Wang and Stedman [137] have recently shown that this restriction in ranks may be obtained by the weaker assumption that only the HT-symmetric part of the effective operator is needed; this follows from only the degeneracy approximation.

Here we generalise the time reversal analysis of Wang and Stedman [137] by including all orders of perturbation; this perturbation refers to the parts of the electronic Hamiltonian that are not exactly solvable (§7.2.1). We also compare the differing results found in the Brillouin-Wigner and Rayleigh-Schrödinger perturbation theories (§7.2.3). As in Chap. 4, we consider the analysis in the Coulomb gauge and find, in contrast to Chap. 4, that different results follow (§7.2.4). In particular, the effective operator in the Coulomb gauge is to be expanded with odd (rather than even) ranks. This surprising result is in direct conflict with that derived by Reid [114] and Wang and Stedman [137] who claim even ranks are required for both gauge choices.

7.2 Judd-Ofelt theory

The following discussion does not require the details of Judd-Ofelt theory. We focus only on the time reversal selection rule which restricts the effective operator to either even or odd ranks (depending on its HT signature). The discussion is therefore of a similar flavour as that given by Wang and Stedman [137].

7.2.1 Brillouin-Wigner perturbation theory

In the electric dipole approximation the electronic part of the one photon absorption transition amplitude is ‘simply’

$$O_{fi\{0\}}^{\{\alpha,\eta\}} \Big|_{\text{OPA}} = \langle f | \mu_\alpha | i \rangle \quad (7.1)$$

(see §2.4.2). The word simply is put in quotes since the evaluation of this amplitude is only possible if the eigenstates of the electronic Hamiltonian, H_{elec} , are known. This is often not the case, and a perturbative expansion of i, f is then needed. As is standard, H_{elec} is written in terms of a solvable part H_0 , where the eigenstates and eigenvalues are known, and a small (by assumption) perturbation V :

$$H_{\text{elec}} = H_0 + V. \quad (7.2)$$

For one photon absorption in lanthanide ions in solids V will contain, for example, the Coulomb repulsion between electrons and the effects of the crystal-field potential arising from the interaction of the ion with the surrounding ligands. If (degenerate) Brillouin-Wigner perturbation theory is employed the expansions of i, f to first order in V are [21]

$$|i\rangle = |i_0\rangle + \sum_{s_0 \notin \mathcal{M}} \frac{|s_0\rangle \langle s_0 | V | i_0 \rangle}{E_{i,s_0}} + \dots, \quad (7.3)$$

$$|f\rangle = |f_0\rangle + \sum_{s_0 \notin \mathcal{M}} \frac{|s_0\rangle \langle s_0 | V | f_0 \rangle}{E_{f,s_0}} + \dots, \quad (7.4)$$

where we have denoted the eigenstates and eigenvalues of H_0 with a subscript 0. We shall assume throughout this chapter that i_0, f_0 are in the same degenerate model space \mathcal{M} , i.e. that \mathcal{M} contains only those states with energy E_{i_0} and that $E_{f_0} = E_{i_0}$ (see for example Lindgren and Morrison [91] for a discussion on model spaces). The condition $s_0 \notin \mathcal{M}$ is therefore equivalent to $E_{s_0} \neq E_{i_0}$. Substituting Eqs.(7.3) and (7.4) into Eq.(7.1) and taking the resulting expression to first order gives

$$\langle f | \mu_\alpha | i \rangle \simeq \langle f_0 | O_{\text{eff}}^{\text{B}} | i_0 \rangle, \quad (7.5)$$

where we have defined an effective operator

$$O_{\text{eff}}^{\text{B}} \equiv \sum_{s_0 \notin \mathcal{M}} \frac{\mu_\alpha | s_0 \rangle \langle s_0 | V}{E_{i,s_0}} + \frac{V | s_0 \rangle \langle s_0 | \mu_\alpha}{E_{f,s_0}}; \quad (7.6)$$

the superscript B indicates Brillouin-Wigner perturbation theory. In Judd-Ofelt theory the zeroth order part, $\langle f_0 | \mu_\alpha | i_0 \rangle$, is zero because the states i_0, f_0 are of identical parity.

As in Eq.(3.51), the HT-symmetrised parts of the effective operator are defined as

$$O_{\text{eff};\pm}^{\text{B}} \equiv \frac{1}{2} \left(O_{\text{eff}}^{\text{B}} \pm \left(\overline{O_{\text{eff}}^{\text{B}}} \right)^\dagger \right). \quad (7.7)$$

The one photon absorption resonance condition gives $E_i + \hbar\omega = E_f$. In the degeneracy approximation, where $\hbar\omega \ll |E_{i,s_0}|$, it follows that the HT-antisymmetric part of the effective operator is smaller than the HT-symmetric part by a factor of $\hbar\omega/E_{i,s_0}$. That is, in the degeneracy approximation the effective operator is equal to its HT-symmetric part plus a small correction which may be neglected [137].

For an operator $\mathcal{O}_q^{(w)}$, of spherical rank w and component q , the matrix element $\langle jm' | \mathcal{O}_q^{(w)} | jm \rangle$ vanishes if $\tau(-1)^w = -1$, where τ is the HT signature of $\mathcal{O}_q^{(w)}$ (see for example Moore and Stedman [103]). Hence, as Wang and Stedman [137] show, if $O_{\text{eff}}^{\text{B}}$ is expanded as a sum of spherical tensor operators only the contributions of even rank are required. This reproduces the result of Judd [68] and Ofelt [108], but without closure assumptions.

7.2.2 Rayleigh-Schrödinger perturbation theory

As indicated by the superscript B, the form of the effective operator in Eq.(7.6) is dependent on the use of Brillouin-Wigner perturbation theory. If instead Rayleigh-Schrödinger theory is employed, a different operator is obtained. In this theory the expansions of i, f to first order are [91]

$$|i\rangle = |i_0\rangle + \sum_{s_0 \notin \mathcal{M}} \frac{|s_0\rangle \langle s_0 | V | i_0 \rangle}{E_{i_0, s_0}} + \dots, \quad (7.8)$$

$$|f\rangle = |f_0\rangle + \sum_{s_0 \notin \mathcal{M}} \frac{|s_0\rangle \langle s_0 | V | f_0 \rangle}{E_{i_0, s_0}} + \dots, \quad (7.9)$$

which differ from Eqs.(7.3) and (7.4) by the use of zeroth order rather than exact energies in the denominators. The effective operator now takes the form

$$O_{\text{eff}}^{\text{R}} \equiv \sum_{s_0 \notin \mathcal{M}} \frac{\mu_\alpha |s_0\rangle \langle s_0 | V}{E_{i_0, s_0}} + \frac{V |s_0\rangle \langle s_0 | \mu_\alpha}{E_{i_0, s_0}}. \quad (7.10)$$

Because the denominators of the two parts of $O_{\text{eff}}^{\text{R}}$ are identical (unlike in $O_{\text{eff}}^{\text{B}}$), the effective operator has an exact HT signature of +1 [140], regardless of any degeneracy approximation. As is now discussed, the HT signature continues to differ between the Brillouin-Wigner and Rayleigh-Schrödinger theories at all orders of V .

In the Rayleigh-Schrödinger and Brillouin-Wigner perturbation theories the exact state i may be written in terms of the wave operators $\Omega_{\mathcal{M}}^{\text{R}}$ and Ω_i^{B} respectively [91, 21]:

$$|i\rangle = \frac{\Omega_{\mathcal{M}}^{\text{R}}|i_0\rangle}{\langle i_0|\Omega_{\mathcal{M}}^{\text{R}\dagger}\Omega_{\mathcal{M}}^{\text{R}}|i_0\rangle^{1/2}} = \frac{\Omega_i^{\text{B}}|i_0\rangle}{\langle i_0|\Omega_i^{\text{B}\dagger}\Omega_i^{\text{B}}|i_0\rangle^{1/2}}; \quad (7.11)$$

the denominators are normalisation factors (as can be seen from Eq.(7.11), the wave operator is defined such that it takes the zeroth order state to the exact state). In the Rayleigh-Schrödinger theory the same wave operator is used for all the states within the model space, and hence the subscript \mathcal{M} . In the Brillouin-Wigner theory the wave operator is dependent on the state under consideration since it is a function of the exact energy corresponding to that state (E_i in this case). A perturbative expansion of the wave operators gives the usual expansions of i (see Eqs.(7.3) and (7.8)). In both theories the wave operator is of the form $P+Q\Theta$, where P is a projection operator onto \mathcal{M} , Q projects onto the orthogonal space and Θ is an operator [91, 21] (by definition, the exact state has a zeroth order part in \mathcal{M} plus a correction in the space orthogonal to \mathcal{M}). Hence,

$$\Omega_{\mathcal{M}}^{\text{R}}|i_0\rangle = \Omega_i^{\text{B}}|i_0\rangle, \quad (7.12)$$

where the presence of the zeroth order state is required, the wave operators themselves are not equivalent. Following directly from Eq.(7.12)

$$\langle f_0|\Omega_{\mathcal{M}}^{\text{R}\dagger}\mu_{\alpha}\Omega_{\mathcal{M}}^{\text{R}}|i_0\rangle = \langle f_0|\Omega_f^{\text{B}\dagger}\mu_{\alpha}\Omega_i^{\text{B}}|i_0\rangle, \quad (7.13)$$

i.e. the matrix elements of the effective operators $\Omega_f^{\text{B}\dagger}\mu_{\alpha}\Omega_i^{\text{B}}$ and $\Omega_{\mathcal{M}}^{\text{R}\dagger}\mu_{\alpha}\Omega_{\mathcal{M}}^{\text{R}}$ are identical (because Eq.(7.12) includes all orders in V , Eq.(7.13) likewise holds to all orders). However, in the Rayleigh-Schrödinger theory it is readily demonstrable that the effective operator has an exact HT signature

$$\left(\overline{\Omega_{\mathcal{M}}^{\text{R}\dagger}\mu_{\alpha}\Omega_{\mathcal{M}}^{\text{R}}}\right)^{\dagger} = \Omega_{\mathcal{M}}^{\text{R}\dagger}\mu_{\alpha}\Omega_{\mathcal{M}}^{\text{R}}, \quad (7.14)$$

whereas in the Brillouin-Wigner theory this is not the case

$$\left(\overline{\Omega_f^{\text{B}\dagger}\mu_{\alpha}\Omega_i^{\text{B}}}\right)^{\dagger} = \Omega_i^{\text{B}\dagger}\mu_{\alpha}\Omega_f^{\text{B}} \neq \Omega_f^{\text{B}\dagger}\mu_{\alpha}\Omega_i^{\text{B}}, \quad (7.15)$$

where $\overline{\Omega_{\mathcal{M}}^{\text{R}}} = \Omega_{\mathcal{M}}^{\text{R}}$, $\overline{\Omega_i^{\text{B}}} = \Omega_i^{\text{B}}$, $\overline{\Omega_f^{\text{B}}} = \Omega_f^{\text{B}}$.

Equation (7.14) is implicit in the analyses of Newman and Balasubramanian [106] and Reid and Richardson [117], since they both state that the most general parameterisation of the effective operator requires (only) even ranks (see the rule stated at the end of §7.2.1). Conversely, Reid [115], who employs Brillouin-Wigner perturbation theory, terms this restriction a “reasonable approximation” (as do Wang and Stedman [137]). To our knowledge Eq.(7.14) is the first explicit HT symmetry-based proof of the exact restriction to even ranks in Rayleigh-Schrödinger theory to all orders in V . The comparison of this with the inexact restriction in the Brillouin-Wigner theory has not been examined previously and is addressed in §7.2.3.

7.2.3 General perturbation theory

Consider some arbitrary scheme for generating the exact states i, f from some known states i_0, f_0 via some generalised wave operators Ω_i^G, Ω_f^G :

$$|i\rangle = \Omega_i^G |i_0\rangle \quad |f\rangle = \Omega_f^G |f_0\rangle. \quad (7.16)$$

The resulting effective operator is $\Omega_f^{G\dagger} \mu_\alpha \Omega_i^G$ (for an extensive discussion on effective operators see Hurtubise and Freed [65]). Under HT the transition amplitude transforms as

$$\langle f_0 | \Omega_f^{G\dagger} \mu_\alpha \Omega_i^G | i_0 \rangle = \langle \bar{i}_0 | \Omega_i^{G\dagger} \mu_\alpha \Omega_f^G | \bar{f}_0 \rangle, \quad (7.17)$$

where we have assumed $\overline{\Omega_i^G} = \Omega_i^G, \overline{\Omega_f^G} = \Omega_f^G$. Hence, the effective operator is HT-even if

$$\Omega_f^G = \Omega_i^G. \quad (7.18)$$

That is, the effective operator may or may not be HT-even depending on the choice of the wave operator, even though the various choices all give identical amplitudes. The finding of §7.2.2 that the effective operator is HT-even in the Rayleigh-Schrödinger but not the Brillouin-Wigner theory may be understood in these terms. In particular, Eq.(7.18) is satisfied in the former because $\Omega_{\mathcal{M}}^R$ is independent of i, f , whereas in the latter $\Omega_i^B \neq \Omega_f^B$.

The conclusion to be drawn from this analysis is that the exact restriction to even ranks is possible (e.g. if Rayleigh-Schrödinger theory is employed) but not guaranteed (e.g. if Brillouin-Wigner theory is employed). However, if the effective operator does contain HT-odd parts, then they must be artifacts of the perturbation theory under consideration in that they cannot be responsible for new predictions. If this were not the case, then, for example, the equally valid Rayleigh-Schrödinger and Brillouin-Wigner theories would contain different physical information.

7.2.4 Coulomb gauge

In the Coulomb gauge the dipole part, \mathbf{p}_C , of the interaction Hamiltonian is

$$\mathbf{p}_C = \sum_{\beta} -\frac{q_{\beta}}{m_{\beta}} \mathbf{p}_{\beta} \quad (7.19)$$

(see Eq.(2.46); we ignore the spin-dependent part). In this gauge the effective operator is of a similar form as in the multipolar gauge, but with \mathbf{p}_C replacing $\boldsymbol{\mu}$. Because \mathbf{p}_C is HT-odd, in Brillouin-Wigner perturbation theory and in the degeneracy approximation the effective operator is principally HT-odd. Similarly, in Rayleigh-Schrödinger theory it is exactly HT-odd:

$$\left(\overline{\Omega_{\mathcal{M}}^R \dagger \mathbf{p}_C \Omega_{\mathcal{M}}^R} \right)^{\dagger} = -\Omega_{\mathcal{M}}^R \dagger \mathbf{p}_C \Omega_{\mathcal{M}}^R. \quad (7.20)$$

Thus, following from the rule stated at the end of §7.2.1, in the Coulomb gauge the effective operator is to be expanded in odd (rather than even) ranks. That is, the spherical ranks required to describe the effective operator depend on the gauge choice.

On the face of it this situation appears similar to that discussed in Chap. 4, where the selection rules found in the nonresonant limit appeared at first glance to be gauge dependent. Indeed, Wang and Stedman [137] (who work with Brillouin-Wigner theory) claim to show that only the HT-even parts of the effective operator are required in the Coulomb gauge. Similarly, Reid [114] appeals to gauge invariance to argue that even ranks are to be employed. The reasoning of Wang and Stedman [137] is analogous to that given in §4.4, where it was verified that the selection rules found in the nonresonant limit are gauge invariant. In particular, the degeneracy approximation involves expanding $O_{\text{eff}}^{\text{B}}$ in a power series in $\hbar\omega/E_{i,s_0}$ and taking the zeroth order part, which is contained in $O_{\text{eff},+}^{\text{B}}$. Because the electric field is proportional to ω times the vector potential, this term is to be compared with the part of the effective operator in Coulomb gauge that is linear in $\hbar\omega/E_{i,s_0}$ (see Eq.(4.50)). However, contrary to the claims of Wang and Stedman [137], both the HT-even and HT-odd parts of the effective operator in Coulomb gauge have contributions that are linear in $\hbar\omega/E_{i,s_0}$. That is, it cannot be argued that only the HT-even part is required, and therefore the restriction to even or odd ranks is dependent on gauge choice. As mentioned, this is also true in Rayleigh-Schrödinger theory where the restriction to even or odd ranks is exact (and so no comparison of powers of $\hbar\omega/E_{i,s_0}$ is possible).

7.3 Future work

The results of this chapter are worthy of further study. Because in Rayleigh-Schrödinger perturbation theory the restriction to even ranks is exact, whereas in Brillouin-Wigner theory it is approximate, we have contended that the odd rank parts in the latter theory are not physically significant. This may be investigated via explicit calculations. The surprising result that the effective operator is to be expanded with odd ranks when working in the Coulomb gauge requires a closer examination. In particular, it must be checked whether this restriction results in different physical predictions. If it is the case then there is necessarily some error in our discussion.

For N -photon absorption (or emission) the associated effective transition operator has an HT signature of $+1$ if all the participating photons are of identical energy (the signature is $(-1)^N$ in the Coulomb gauge). Thus, the results of this chapter will hold equally well if μ is replaced by $O_{fi\{0\}}^{\{\alpha,\eta\}}|_{\text{NPA}}$. Two photon absorption in lanthanides has been carefully studied by various workers [116] and is therefore an ideal example to test this claim; particularly relevant here is the two photon absorption circular intensity difference process discussed in §5.2.4.

Finally, and somewhat more speculatively, we note that coherent nonlinear optical processes require only the HT-symmetric part of the effective transition operator (Eq.(3.57); this same restriction holds in the Coulomb gauge). This restriction holds at all multipole levels and also holds regardless of the presence of intermediate resonances. Hence, as in the case of N -photon absorption, it may be possible to apply the results of this chapter to such processes by replacing $\boldsymbol{\mu}$ with $\text{Av}_i O_{ii\{\mathbf{k}\}+}^{\{\alpha,\eta\}}$. (Second-harmonic generation in rare earth crystals has been examined by Karmakar *et al.* [74].)

8. Conclusions

If you look carefully, you will see that the concept (of parity) is not used once in my book – Dirac [127].

8.1 Summary of results

In this thesis we have considered the nonlinear optical interaction of a system of identical particles (e.g. molecules, atoms, ions, electrons) with a quantised radiation field. The particular quantity under examination is the light scattering intensity, which is found using Fermi's Golden Rule. By assuming the particles are independent, the intensity has been expressed in terms of one-particle transition amplitudes; this simplification has been carried out explicitly because standard treatments appear not to adequately handle degeneracies in the particles' initial and final states. The notation used to describe these amplitudes allows the results of this thesis to be clearly presented. Throughout this thesis, unless otherwise specified, we have worked in the multipolar gauge, all multipole terms have been included, and intermediate resonances have been allowed for by the use of phenomenological damping factors.

The findings of this thesis have followed from the application of time reversal symmetry to these one-particle amplitudes when a statistical average is required (i.e. when T-conjugate electronic states are initially equally populated). In particular, HT symmetry has been applied to the electronic parts of the transition amplitude in Chaps. 4, 6, 7 and the second half of Chap. 3, and T symmetry to the electronic parts of the full scattering intensity Chap. 5. Results following from this extend analyses in Rayleigh (and Raman) scattering to arbitrary order processes. Further, by the inclusion of damping factors and all multipole terms, previous results applicable to nonlinear optics have been generalised.

The application of H, T and HT to the transition amplitude of a general nonlinear optical process gives the reciprocity, conjugation and reversal theorems. Our contribution has been to incorporate phenomenological damping factors. This generalisation has been crucial since in this thesis we have considered processes involving intermediate resonances. Our derivation also allows relativistic corrections to be readily incorporated; the spin-orbit interaction has been explicitly included in a gauge invariant manner. We allow for arbitrary phase choices

associated with the action of T on the photon field, and conclude that a non-standard convention gives the simplest expressions. It is checked that this phase convention does not affect the canonical quantisation of the electromagnetic field.

By splitting the effective transition operator into HT-symmetrised parts, Onsager relations are derived for self-conjugate processes. They generalise those found for Rayleigh scattering in that they are applicable to certain nonlinear optical processes such as those four wave mixing processes in which the two output photons have identical energies to the two input photons. The Onsager relations derived correct Bungay *et al.* [22], who incorrectly claim the relations are violated by the presence of spin-orbit coupling. The error in Bungay *et al.* [22] is their omission of a statistical average; their Onsager-violating terms cancel on performing such an average.

The time reversal selection rules which follow when the nonresonant limit is valid (where the photon frequencies are scaled down towards zero) have been examined in detail. Some general results are derived; these are considered in the specific cases where only the lowest order multipole contributions are included. It is found that the magnetic dipole terms in coherent processes are suppressed, whereas the electric quadrupole terms are not. This modifies the belief that magnetic dipole terms are generally an order of magnitude larger than the electric quadrupole terms (e.g. Cao and Zhu [28]). For transitions between T -conjugate states in Kramers systems the electric dipole and quadrupole terms are suppressed whereas the magnetic dipole terms are not; this second rule is derived without assuming a statistical average. These rules allow for an estimation of the relative importance of the various multipole contributions in the nonresonant limit. The behaviour of these rules in regions slightly outside the nonresonant limit is also examined. It is found that the convergence to Kleinman symmetry is quadratic rather than linear in the scaling parameter. This extends the discussion of Levine [89], who has previously obtained this result for sum-frequency generation. If the analysis is carried out in the Coulomb gauge, the results which follow appear at first glance to be inequivalent to those outlined above. The verification that identical rules are found for both gauge choices is nontrivial; the correct rules are found most directly in the multipolar gauge.

Previous analyses have shown that purely electric dipole contributions to natural optical activity are possible in Rayleigh and Raman scattering [62] and in second-harmonic generation [27] if damping factors are included. We have shown that the conjugation theorem requires this intensity difference to exist for all processes. The magnitude of the purely electric dipole contribution has been compared with the magnitude of the traditional contribution involving the interference of the electric and magnetic dipole parts of the transition amplitude. In agreement with previous discussions [27, 62], we find that in the presence of strong intermediate resonances the former contribution dominates over the latter. For moderate resonances we find that the former contribution is still of importance, contrary to the claims of Kauranen *et al.* [75] and Maki *et al.* [97]. We note that it ought to be possible to combine the experimental methods of Gunde and Richardson [54]

and Huang *et al.* [64] to measure natural optical activity in resonant two photon absorption. Standard parity selection rules are significantly modified when the purely electric dipole contributions are involved. In particular, natural optical activity in forward Rayleigh scattering in fluid media no longer requires the constituent molecules to be chiral.

In the case of weak resonances the simplest expedient for dealing with singular energy denominators is to incorporate within each denominator factor a small imaginary addendum, expressedly for the purpose of obtaining the desired analytic properties. We have examined the restrictions the reversal theorem places on the signs that may be associated with these addenda. In particular, a derivation of this theorem is presented that allows for interacting particles and includes all degrees of freedom, thus proving that the addenda must be included in such a manner as to preserve this theorem. This analysis, in combination with certain non-phenomenological discussions of damping [8, 34], leads us to adopt a prescription where the signs are all identical. The damping signs usually associated with the semiclassical optical susceptibility formalism have a time-ordered sign prescription [19, 23, 41, 87, 121], and are in conflict with the reversal theorem. This prescription is therefore incorrect. We show that the reciprocity and conjugation theorems need not in general relate two physical processes. Hence, although in the time-ordered sign prescription reciprocity relates two physical processes, whereas it does not in the fixed sign prescription, this does not constitute support for the former prescription. In most cases the difference in results found under the two prescriptions is small; however, in a few cases qualitative differences in prediction can arise, which are particularly amenable to experimental test. We show that electrooptic rotation in fluid media is an example.

In Judd-Ofelt theory the effective operator for one photon absorption within the $4f^n$ configuration is expanded as a sum of spherical tensors. We have shown that if Rayleigh-Schödinger perturbation theory is employed, only the even ranks are required. Although this result is standard, to our knowledge we have given the first explicit HT symmetry-based proof of this exact restriction to all orders of perturbation. The comparison of this result with the corresponding analysis in Brillouin-Wigner perturbation theory has been examined. In this theory the restriction to even ranks is inexact and we conclude that the odd rank parts are an artifact of that theory. In general the exact restriction to even ranks will not hold unless the wave operators satisfy special conditions. If the derivations are carried out in the Coulomb gauge, the restriction is now to odd ranks. This surprising result is in direct conflict with that derived by Reid [114] and Wang and Stedman [137] who claim even ranks are required for both gauge choices. However, we show those discussions are incorrect.

8.2 Future work

In Chap. 3 it was shown that only the HT-symmetric part of the effective transition operator is needed to describe coherent processes. Following from this, nonlinear optical Onsager relations and certain selection rules (in Chap. 4) were derived. In the case of incoherent processes both the symmetric and antisymmetric parts are required. Therefore, the properties of the light scattering intensity depend on whether the process under consideration is coherent or incoherent. Indeed, it may be the case that if the optical rotation measured in Zheludev *et al.* [143] involved (slightly) incoherent scattering, then the parts of the amplitude that are linear in the wavevector could in fact be nonzero. Such significant differences in the behaviour of coherent and incoherent processes are worthy of further study. Also, such a study may provide a check on the validity of our reduction of the light scattering intensity into one-particle transition amplitudes (given by Eqs.(2.7) to (2.9)).

The analysis in Chap. 5 on natural optical activity in resonant two photon absorption may be expanded. First, the restrictions the relevant point group symmetry places on the process have not been considered. Second, the assumption that the damping factors for parity-conjugate states are equal needs to be investigated. Third, the numerical analysis of Gunde *et al.* [53] on the experimental data in Gunde and Richardson [54] may be extended to allow for purely electric dipole contributions. This could also relate to a detailed modelling of the relative importance of the electric dipole and traditional contributions to the intensity difference (our estimate is that strong resonances are not required for the domination of the electric dipole contributions; see Eq.(5.17)).

As discussed in Chap. 6, an analysis of damping based on a first principles calculation is generally intractable. However, in a few simple cases a nonphenomenological approach may be possible. For example, Cohen-Tannoudji *et al.* [34] derive the form of the transition amplitude for resonant Rayleigh scattering by a single molecule when radiative damping is present. For this simple system it may be possible to extend that analysis to cover second-harmonic generation, and therefore prove in detail that the fixed sign prescription is appropriate (Andrews *et al.* [8] discuss this issue in general terms). Such an explicit confirmation would be of benefit since the time-ordered sign prescription is widely employed in the nonlinear optics literature.

The results of Chap. 7 raise interesting questions that are worthy of further study. As described in §7.3, the findings need to be tested via explicit calculations. Also, it is proposed that these results applicable to one photon absorption be extended to higher order processes.

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